

AD-A071 717

FLORIDA UNIV GAINESVILLE ENGINEERING AND INDUSTRIAL--ETC F/6 7/4  
ELECTRICALLY CONTROLLED COLORATION OF MATERIALS.(U)  
JUN 79 P H HOLLOWAY, R E HUMMEL

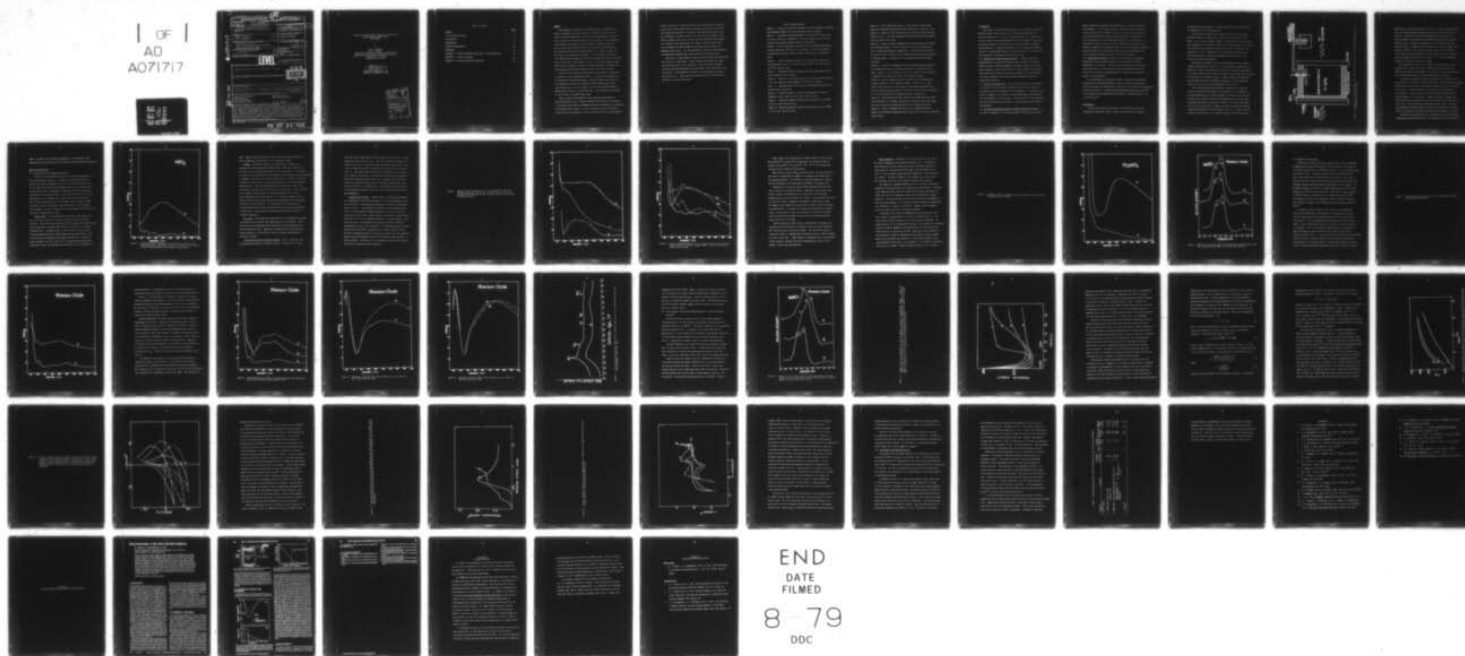
DAA629-76-G-0151

UNCLASSIFIED

ARO-13056.1-P

NL

| OF |  
AD  
A071717



END  
DATE  
FILMED

8-79  
DDC



NATIONAL BUREAU OF STANDARDS  
MICROCOPY RESOLUTION TEST CHART

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

## REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS  
BEFORE COMPLETING FORM

1. REPORT NUMBER 19 13056.1-P	2. CONT. ACCESSION NO. 18 AR9	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ELECTRICALLY CONTROLLED COLORATION OF MATERIALS		5. TYPE OF REPORT & PERIOD COVERED Final Report Jan 76 - Mar 79
7. AUTHOR(s) Paul H. Holloway Rolf E. Hummel		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Florida Dept. of Materials Science & Engineering Gainesville, Florida 32611		8. CONTRACT OR GRANT NUMBER(s) DAAG29-76-G-0151
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 12 61p
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE Jun 79
LEVEL		13. NUMBER OF PAGES 58
		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) DDC RECEIVED JUL 26 1979 C		
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) coloration of materials solid materials electric potentials thermochromic effects electrolyte cells electrolyte materials 139 950		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report presents the results of a study of the phenomena of coloration of solid materials by application of electric potentials. Four specific aspects of this subject have been emphasized. First, new electrochromic materials were surveyed. Second, rhenium oxides were studied in detail to determine the origin of their thermochromic effect. Third, the rate-controlling mechanisms in liquid electrolyte cells were investigated. And fourth, various solid-state electrolyte materials were studied and one - termed PSSE - gave improved performance over those previously discussed in the literature.		

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

79 07 24 063

A071717

DDC FILE COPY

"Electrically Controlled Coloration of Materials"  
January, 1976 - March, 1979  
Final Report

by

Paul H. Holloway  
Rolf E. Hummel

Department of Materials Science and Engineering  
Engineering and Industrial Experiment Station  
University of Florida  
Gainesville, FL 32611

Prepared for the  
U.S. Army Research Office  
Physics Branch  
Research Triangle Park, NC  
Contract No. DAAG29-76-G-0151

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DDC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or special
A	



## Table of Contents

	<u>Page</u>
Summary	1
List of Figure Captions	3
Introduction	5
Experimental	6
Results and Discussion	10
References	50
Appendix 1: "Electrochromism in $\text{WO}_3$ Films with BaO Additions"	53
Appendix 2: Project Personnel	56
Appendix 3: Publications and Presentations	58

### Summary

The phenomena of coloration of solid materials by application of electric potentials have been studied. Four specific aspects of this subject have been emphasized in our work at the University of Florida. First, new electrochromic materials have been surveyed. We established that rhenium oxide displays the electrochromic phenomena along with several metal tungstates and vanadium and tungsten phosphate glasses. Our current studies have shown that addition of a number of oxides to  $WO_3$  results in a decreased EC response. All of the materials studied have shown absorption maxima near 100 nm and minima near 500 nm, therefore they have all been various shades of blue. However some mixtures showed shifts in the wavelength of absorption maxima suggesting the possibility of developing electrochromic materials with colors other than blue.

Second, we have studied rhenium oxides in more detail to determine the origin of their thermochromic effect. The data show that  $Re_2O_7$  may be deposited by heating either  $ReO_2$  or  $ReO_3$  in vacuum.  $Re_2O_7$  films are very hygroscopic and must be passivated towards adsorption of water. Upon heating  $Re_2O_7$  in air or vacuum, a blue film is produced because of decomposition of  $Re_2O_7$  to crystalline  $ReO_3$ . This may also be the origin of the EC effect in rhenium oxide films.

Third, we have investigated the rate-controlling mechanisms in liquid electrolyte cells. The data indicate that the rate of coloration is initially controlled by a phenomenon that can be modelled as a resistance in the Butler-Volmer equation. After long times ( $\sim 1$  sec.) the control switches from this mechanism to control by diffusion across the Helmholtz

layer in the EC cell. The initial rate of coloration may be controlled by the rate at which protons can be injected into the  $\text{WO}_3$  film, and we have found that deposition of a porous conducting surface layer on the  $\text{WO}_3$  considerably increases the rate of coloration and bleaching. This effect probably results from the fact that the conducting layer changes the electronic band bending near the surface of the  $\text{WO}_3$  layer, and it also increases the field strength in the electrolyte to negate the Helmholtz layer effect. We have optimized the conducting layer material and deposition technique and a patent application has been filed.

And fourth, we have studied various solid-state electrolyte materials and found one - termed PSSE - to give improved performance over those previously discussed in the literature. With PSSE we have obtained coloration and bleaching speeds ten times faster than reported for other electrolytes. These speeds are similar to those obtained for liquid electrolyte cells. These data and processing steps for PSSE have been described in a patent disclosure.

## List of Figure Captions

Figure 1. Schematic of an electrochromic cell used to measure coloration and bleaching response of an electrochromic film (e.g.  $\text{WO}_3$ ).

Figure 2. Absorbance versus wavelength for a  $\text{WO}_3$  film (A) before and (B) after coloration. Absorbance =  $\log(I_0/I)$ , where  $I_0$  and  $I$  are the incident and transmitted beam intensity, respectively.

Figure 3. Optical absorption spectra for (V) an as-deposited 80%  $\text{V}_2\text{O}_5$ -20%  $\text{P}_2\text{O}_5$  glass film and (VC) its colored state. Curve (g) represents the glass with 2%  $\text{V}_2\text{O}_5$ , 5%  $\text{MoO}_3$ , 61%  $\text{WO}_3$ , and 32%  $\text{P}_2\text{O}_5$  in uncolored state.

Figure 4. Optical absorption spectra for (V)  $\text{V}_2\text{O}_5$ - $\text{WO}_3$  films in the uncolored state and (h) for the heat treated films. (VC) and (hc) are for the EC colored films.

Figure 5. Absorbance spectra of  $\text{Re}_2\text{WO}_4$  film (A) as-deposited and (B) after coloration with 1 N  $\text{H}_2\text{SO}_4$ .

Figure 6. ESCA Re 4f core level spectra from (A)  $\text{Re}_2\text{O}_7$  powder and from films vapor deposited from powders of (B)  $\text{ReO}_3$  and (C)  $\text{ReO}_2$ .

Figure 7. Absorbance spectra for  $\text{Re}_2\text{O}_7$  (A) as-deposited and (B) after electrochromic coloration.

Figure 8. Absorbance spectra of  $\text{Re}_2\text{O}_7$  (A) as-deposited and after heating in air at  $150^\circ\text{C}$  for (B) 0.5 min. and (C) 1 min.

Figure 9. Absorbance spectra of  $\text{Re}_2\text{O}_7$  after heating in air at  $150^\circ\text{C}$  for (A) 1.5 min. and (B) 2 min.

Figure 10. Absorbance spectra of  $\text{Re}_2\text{O}_7$  after heating in air at  $150^\circ\text{C}$  for (A) 3 min. and (B) 11 min.



Figure 11. X-ray diffraction spectra of  $\text{Re}_2\text{O}_7$  film on soda-silicate glass (A) as-deposited and (B) after heat treatment at  $150^\circ\text{C}$  for 2 min.

Figure 12. ESCA Re 4f core level spectra for (A)  $\text{Re}_2\text{O}_7$  powder, (B)  $\text{ReO}_3$  powder, and (C) a film vapor deposited from  $\text{ReO}_2$  and colored by heating in air at  $150^\circ\text{C}$  for 0.5 min.

Figure 13. Change in optical transmission at 900 nm during a coloration and bleaching sequence. Curves (a) and (b) refer to  $\text{WO}_3$  without and with a conducting overlayer, respectively. Curves (c) and (d) refer to  $\text{WO}_3$  with +0.5 and -0.5 volts on the conducting surface layer with respect to the  $\text{SnO}_2$  layer, in addition to 1.5 V between the  $\text{SnO}_2$  and counter electrode.

Figure 14. Current (I) changes with time during coloration normalized to the initial current ( $I_0$ ) versus the inverse of the square root of time. Curves a, b, and c refer to +0.6, +0.4, and +0.1 volts respectively applied to  $\text{SnO}_2$  and referenced to the calomel electrode.

Figure 15. Cyclic voltametry curves of current versus potentiostatic voltage referenced to the calomel electrode. Curves a, b, c, and d refer to  $\text{WO}_3$ ,  $\text{WO}_3$  with an electrically floating conducting layer,  $\text{WO}_3$  with the conducting layer shorted to the  $\text{SnO}_2$  layer, and with a potential of -0.1 volts applied to the conducting layer, respectively.

Figure 16. The variation of photo current with voltage applied to  $\text{SnO}_2$  and referenced to the calomel electrode for (a)  $\text{WO}_3$  on  $\text{SnO}_2$  coated glass and for (b)  $\text{WO}_3$  with a conducting layer in 0.5 N  $\text{H}_2\text{SO}_4$  electrolyte.

Figure 17. Cyclic voltametry curves for (a) a conducting layer on glass, (b) a nonporous conducting layer on  $\text{WO}_3$ , and (c) a porous conducting layer on  $\text{WO}_3$ .



## Introduction

This final report describes the results of a three-year study into materials whose colored state can be altered by application of an electric potential (i.e. exhibit an electrochromic - EC - effect) and into the rate-controlling mechanisms of this color change. EC materials have great potential for display devices, and the ability to adapt a certain material to design requirements (i.e. environment and speed) is critical to technological success in the display area. As a result the study has been concentrated in four specific areas.

(1) Survey of new electrochromic materials. We have successfully demonstrated that rhenium and vanadium oxides, mixtures of  $WO_3$  with rhenium, barium, rubidium, vanadium, and bismuth oxides, and several metal tungstates exhibit the EC effect. These materials were surveyed qualitatively for stability and spectral response. The data indicate that metal tungstates and vanadium-tungsten-phosphate glasses are promising EC materials.

(2) Studies of rhenium oxide. The EC and thermochromic (TC) behavior of powdered and vapor deposited rhenium oxides have been studied to determine the connection between EC and TC behavior. The stability and spectral response of the oxides have been measured and correlated with the oxide composition and structure. The data indicate that electrochromism and thermochromism are related to crystalline structure changes in this material.

(3) EC rate-controlling mechanisms in liquid electrolyte devices. To be used, for example, as a wristwatch display, EC materials must have

faster coloration and bleach (C/B) times than are currently reported in the literature. In the present work, we found that metal overlayers on the  $\text{WO}_3$  could result in faster C/B times. A patent has been filed to protect the University's rights to this discovery.<sup>1</sup> In addition, we have investigated the rate-limiting mechanisms of coloration which are influenced by these overlayers. We have studied electrochemical cell kinetics, composite cell configurations, and current-voltage relationships. The data indicate that electrolyte double layers,  $\text{WO}_3$  impedance, and surface Schottky barriers all play a role in EC coloration.

(4) Solid-state EC devices. Because of some possible technological advantages, we have surveyed various solid electrolytes for their application in EC devices. The intent was to decrease the C/B times of solid-state cells. One electrolyte worked exceptionally well in the devices, and a patent is being applied for to protect the University's rights to this discovery.<sup>2</sup>

In the remainder of this report we will first discuss experimental techniques and procedures pertinent to all four areas, then present in detail the results for these areas. Discussion of the results is incorporated within each section. In addition some experimental details are included in the results section where they are pertinent to the objectives of one of the four areas.

### Experimental

With divergent specific objectives in the above four areas, the experimental procedures varied. However certain procedures common to

all areas are discussed here. Procedures specific to a given area may be discussed in the following section.

The starting materials used in this study were all commercially available powders from Cerac, Inc. (oxides and tungstates), or from McKay, Inc., or Alpha Inorganic (metals). Those used as thin films were vapor deposited from a heated crucible onto an oxide substrate. Generally this substrate was glass with a coating of  $\text{SnO}_2$  (i.e. NESA glass, PPG Industries). Prior to deposition, the substrates were cleaned with detergent and water, rinsed with deionized water and alcohol, then placed in the deposition system.

Depositions were made in an oil diffusion pumped, liquid nitrogen trapped vacuum system at  $\lesssim 5 \times 10^{-3}$  Pa. The system was not baked prior to deposition, however the oxide source material was generally outgassed at a low power setting with a shutter protecting the substrate from deposition. The substrates were normally heated to  $\sim 100^\circ\text{C}$ , however some deposition was performed without such substrate preheating. Typical deposition rates were  $\sim 2$  nm/s and film thicknesses were  $\sim 0.2$ – $0.6$   $\mu\text{m}$ .

The electrochromic and thermochromic response of the films was generally characterized by measuring the absorption in transmission. A Cary spectrophotometer was used to measure the response from 200 nm to  $\sim 2000$  nm, and a Bausch and Lomb spectrophotometer was used for single wavelength measurements, typically at  $\sim 800$  nm. For liquid electrolyte cells, the electrolyte was 1 N  $\text{H}_2\text{SO}_4$ , and the coloration and bleaching response was measured in the cell shown in Fig. 1. A Luggin capillary connects the electrolyte to a saturated calomel reference electrode. A



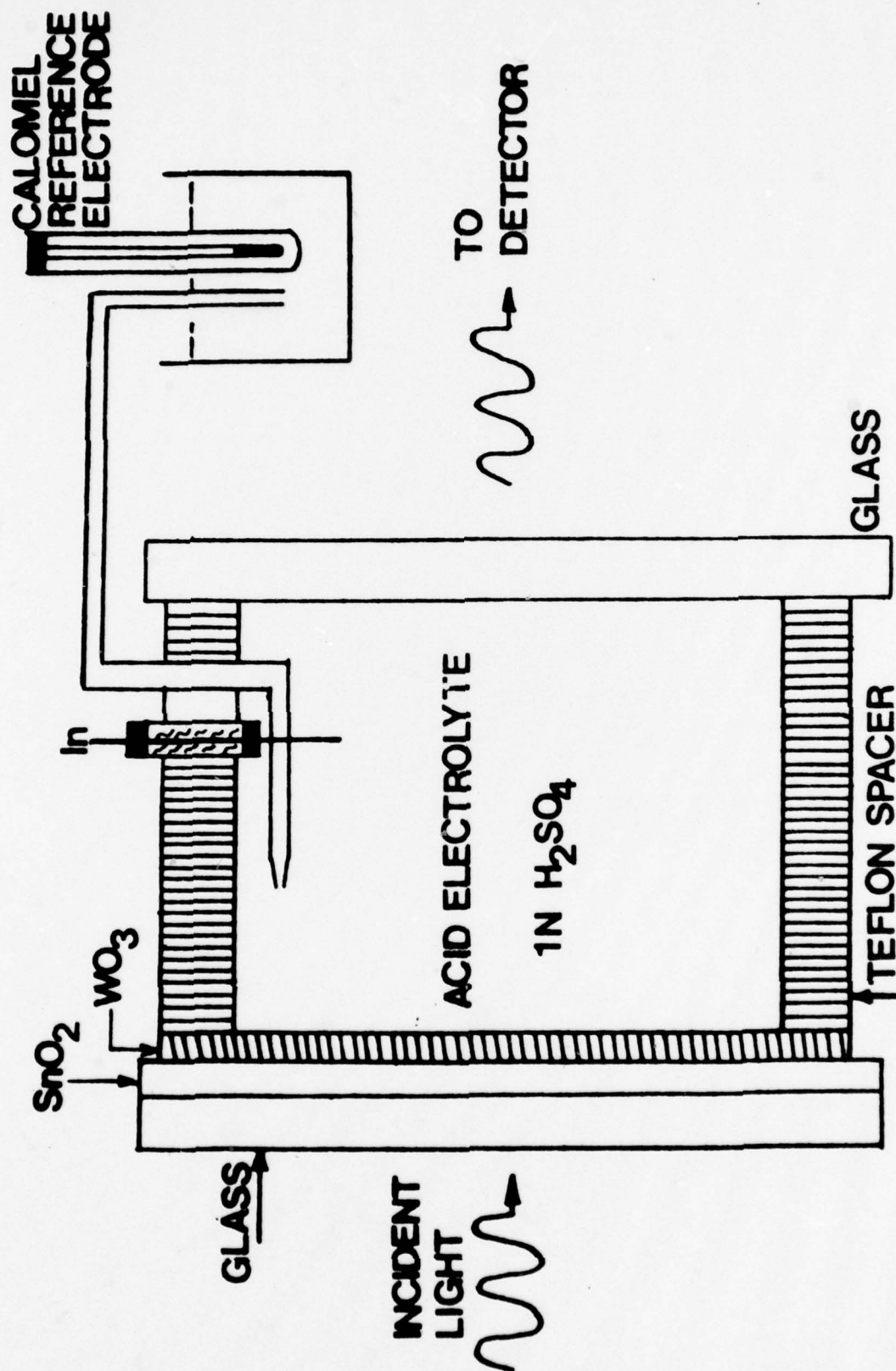


Figure 1. Schematic of an electrochromic cell used to measure coloration and bleaching response of an electrochromic film (e.g.  $WO_3$ ).

metal counter electrode is mounted in the cell. In some cases reflection data were recorded simply by moving the detector around to the front of the film. Non-specular reflection was measured at an angle of  $\sim 30^\circ$ . Current flowing through the EC cell was measured and plotted along with absorption data, allowing a determination of the coloration per unit injected charge. Voltages were often supplied by constant voltage power supplies. However in the critical kinetic studies, the cells were EC colored using either galvanostatic or potentiostatic control, with the saturated calomel electrode as a reference. The counter electrode was normally Pt, although In was used at times.

To qualitatively check the EC response, some films were colored directly with 1 N  $\text{H}_2\text{SO}_4$  into which an indium wire was inserted. As reported by Crandall and Faughman,<sup>3</sup> this caused EC coloration presumably due to electrons injected by indium dissolution into the  $\text{H}_2\text{SO}_4$ .

The powders and deposited films were characterized chemically and structurally by a number of different techniques. Rutherford backscattering (RBS)<sup>4</sup> and particle induced x-ray emission (PIXE)<sup>4</sup> were used to determine the quantity of elements present and to analyze the stoichiometry of oxides present. Auger electron spectroscopy (AES)<sup>4</sup> was also used for elemental analysis on the surface. Elemental analysis throughout the film thickness was performed with AES in conjunction with sputtering by argon ions. X-ray photoelectron spectroscopy (XPS or ESCA - electron spectroscopy for chemical analysis)<sup>4</sup> was used to determine the chemical state of the oxides at the surface and after sputtering into the films.

Structural characterization was accomplished by optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy



(TEM). For TEM, thin EC films were deposited on thin graphite films simultaneously with deposition on the previously described glass substrates.

### Results and Discussion

#### (1) Survey of new electrochromic materials

Our work on the electrochromic effect has centered on mixtures of  $\text{WO}_3$  with  $\text{BaO}$ ,  $\text{Re}_2\text{O}_7$ , and  $\text{V}_2\text{O}_5$ . In addition we have studied the EC character of several tungstates (e.g. Ca, Sr, Ba, Ce, Rb, Na, Bi, Mg, Co, Mn, and Ni) and shown that the powder form of most of these can be electrically colored. Furthermore, tungstates of Ba and Sr have been deposited as thin films and shown to color electrically, but not to the same degree as in the powder form. Based upon Sakka's photochromic data,<sup>5</sup> we have added  $\text{Bi}_2\text{O}_3$  to both the powder and thin films of  $\text{BaWO}_4$  and  $\text{SrWO}_4$  to induce a different colored EC material. While dramatic color changes (e.g. blue to red) have not been produced, we have produced films with varying shades of blue.

Single oxides. The electrochromic oxides ( $\text{WO}_3$ ,  $\text{MoO}_3$ ,  $\text{Re}_2\text{O}_7$ , and  $\text{V}_2\text{O}_5$ ) have been studied as a basis for comparison with mixed oxide materials.  $\text{WO}_3$  and  $\text{MoO}_3$  were transparent after deposition and electrically colored deep blue, consistent with literature data (see, for example, references 6-8). As shown in Fig. 2, blue coloration in  $\text{WO}_3$  results from strong absorption over a broad range centered near 1000 nm.  $\text{V}_2\text{O}_5$  was light brown as deposited and turned blue-green after coloration, again consistent with the literature.<sup>8,9</sup> Deposited rhenium oxide was translucent yellow, but switched upon application of a dc potential to

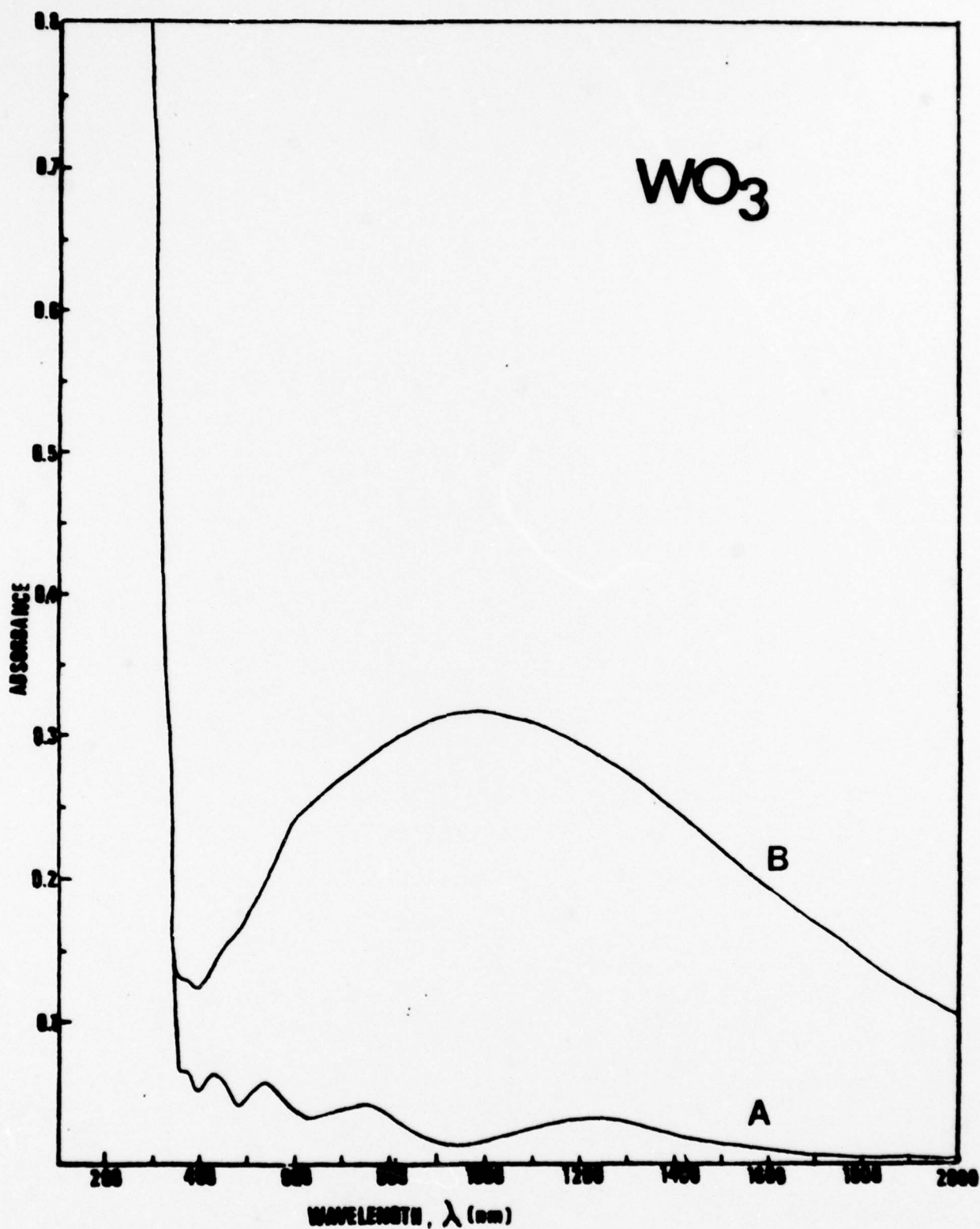


Figure 2. Absorbance versus wavelength for a WO<sub>3</sub> film (A) before and (B) after coloration. Absorbance =  $\log(I_0/I)$ , where  $I_0$  and  $I$  are the incident and transmitted beam intensity, respectively.

blue. This is the first report of the EC effect in rhenium oxide and it will be discussed in more detail in the subsequent section.

BaO-WO<sub>3</sub>. Mixed-oxide films of the system  $x\text{WO}_3 + (1-x)\text{BaO}$  were prepared by co-evaporating  $\text{WO}_3$  and BaO powders. Addition of BaO to  $\text{WO}_3$  was found to have an inhibiting effect on color development. For example, 10 atomic % barium reduced the total amount of light absorbed electrochromically as compared to pure  $\text{WO}_3$ . For barium concentrations of <10% the coloration inhibition is small, but at concentrations greater than 40% the inhibition approaches 90%. Films with approximately 10% barium were found to have a deep blue coloration upon removal from the vacuum system. This coloration can be removed by application of a bleaching potential of 1.5 volts. Sharp peaks were found in the diffuse x-ray diffraction patterns of the films at barium concentrations greater than approximately 45%, indicating the onset of crystallization. It is believed that the presence of a crystalline BaO phase is partly responsible for the coloration inhibition in these films. These results are described in reference 10 which is attached in Appendix 1.

Re<sub>2</sub>O<sub>7</sub>-WO<sub>3</sub>. Vapor-deposited films prepared by co-evaporation underwent a reversible blue coloration upon application of a dc potential. These films were quite deliquescent and therefore may be more appropriate for a solid-electrolyte cell. Additions of rhenium oxide to  $\text{WO}_3$  resulted in strong inhibition of the EC effort even for rhenium concentrations of less than 10 atomic %.

V<sub>2</sub>O<sub>5</sub>-P<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub>-P<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>-WO<sub>3</sub> glasses. Melts of 80% V<sub>2</sub>O<sub>5</sub> : 20% P<sub>2</sub>O<sub>5</sub> glasses were made in a platinum crucible at 1200°C in air. They

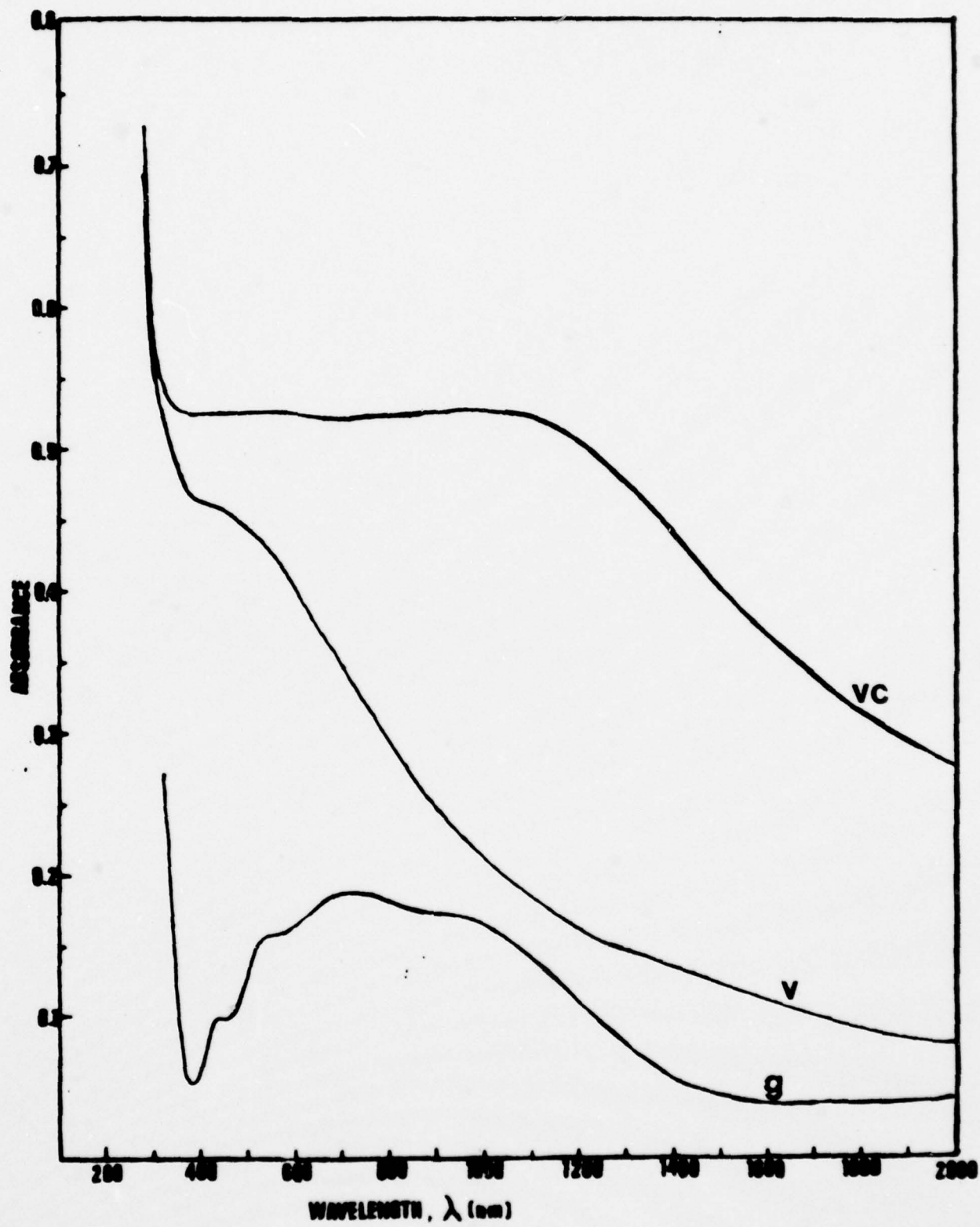
were cast onto a copper plate and heat treated at 250°C for 4 h. These glasses were dark brown in color. They were thermally evaporated at a pressure of  $10^{-1}$  Pa to form transparent films with a brown color. They could be reversibly colored to blue-brown by application of a voltage (Fig. 3). Glass melts were also made with a composition of 2%  $V_2O_5$ , 5%  $MoO_3$ , 61%  $WO_3$ , and 32%  $P_2O_5$ . The bulk glass was blue, and evaporated films were transparent with a blue color. Although they could be EC colored to a deeper blue and could be bleached to a light blue, they would not bleach to a colorless film. The absorption spectra (Fig. 3) of this glass shows peaks at 400, 500, 700, and 900 nm with the 700 nm peak dominating.

$V_2O_5-WO_3$  and  $V_2O_5-MoO_3$ . Films of  $xWO_3 + (1-x)V_2O_5$  were deposited by co-evaporation from different sources. These  $V_2O_5$  additions to  $WO_3$  have the effect of decreasing the band edge as shown in the absorption spectra in Fig. 4. Electrochromic coloration of these mixtures gives rise to a broad absorption peak extending from 0.65–1.2  $\mu m$  (Fig. 4), resulting in a blue color. Apart from the characteristic electrochromic peak at 0.9 to 1.0  $\mu m$ , an additional peak at 0.7  $\mu m$  was observed. This peak was found to increase when the films were heated to  $\sim 250^\circ C$  for approximately one hour after deposition. The band edge shifted to lower energies with increasing  $V_2O_5$  additions in a manner similar to that reported by Bogomolova *et al.*<sup>11</sup> for  $WO_3-P_2O_5$  glasses with  $V_2O_5$  additions. However upon electrochromic coloration the band edge seems to shift to higher energies. Absorption in the transmission window between 250 and 550 nm also increased with  $V_2O_5$  additions.



Figure 3. Optical absorption spectra for (V) an as-deposited 80%  $V_2O_5$ -20%  $P_2O_5$  glass film and (VC) its colored state. Curve (g) represents the glass with 2%  $V_2O_5$ , 5%  $MoO_3$ , 61%  $WO_3$ , and 32%  $P_2O_5$  in uncolored state.





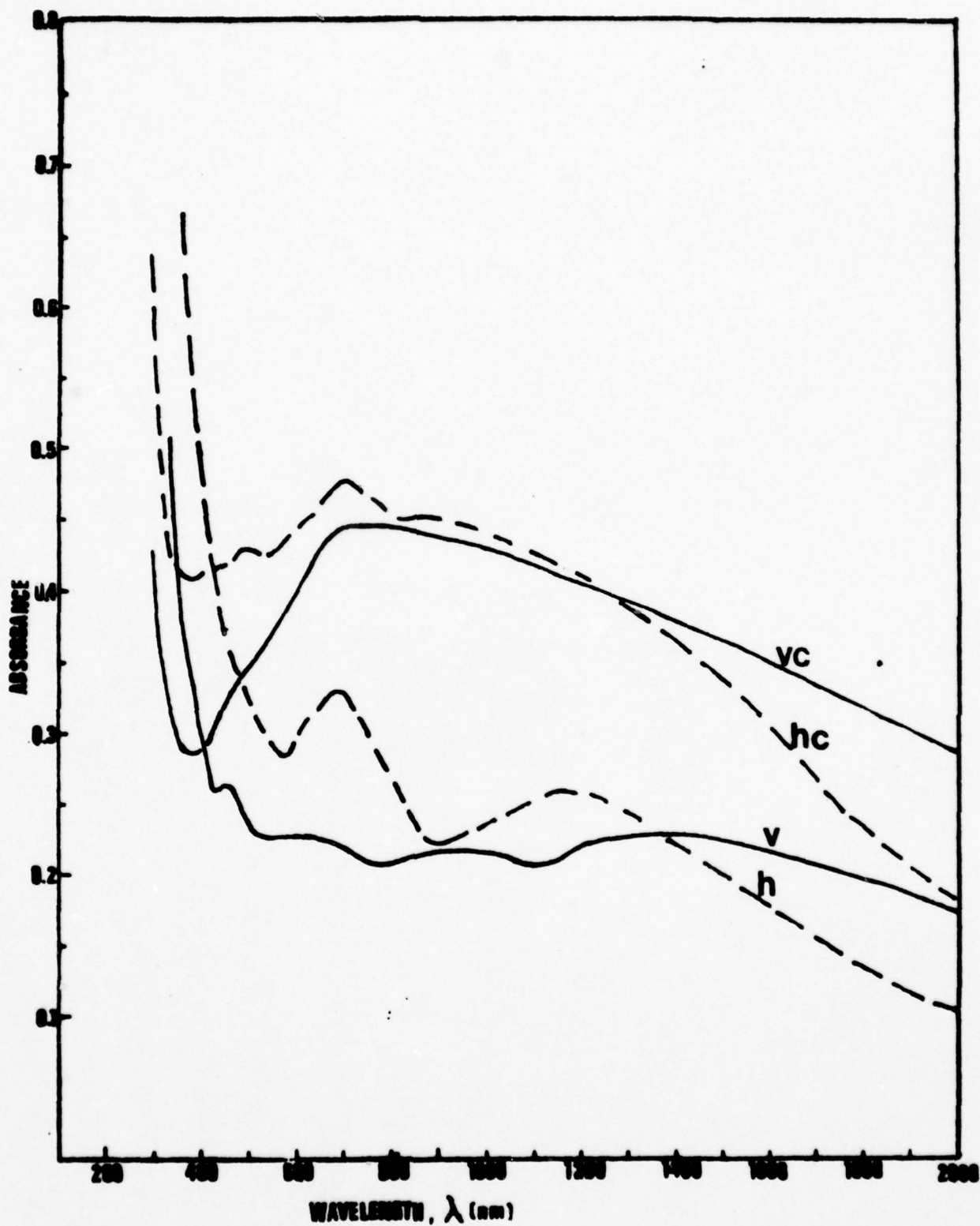


Figure 4. Optical absorption spectra for (v)  $V_2O_5-WO_3$  films in the uncolored state and (h) for the heat treated films. (vc) and (hc) are for the EC colored films.

These results can be explained in a manner similar to that for  $\text{WO}_3$ - $\text{MoO}_3$  mixtures<sup>12</sup> by saying that the absorption in the mixed oxides is caused by excitations of the type  $\text{W}^{5+} + \text{V}^{5+} \rightarrow \text{W}^{6+} \text{V}^{4+}$  and excitations increase with the degree of EC coloration.

Mixed films of  $\text{V}_2\text{O}_3$  and  $\text{WO}_3$  were also studied. The deposited films were grey but transparent as compared to transparent and light yellow for  $\text{V}_2\text{O}_5$ - $\text{WO}_3$  mixtures. EC coloration of  $\text{V}_2\text{O}_3$ - $\text{WO}_3$  resulted in a peak at  $\sim 900$  nm and changes in the band edge were similar to  $\text{V}_2\text{O}_5$ - $\text{WO}_3$  films.

Although all the  $\text{V}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  mixtures produced a blue EC color, their coloration rates were different. Additions of  $\text{V}_2\text{O}_5$  and  $\text{V}_2\text{O}_3$  were found to reduce the dissolution of the films into the electrolyte, although pure  $\text{V}_2\text{O}_5$  was not stable in 1 N  $\text{H}_2\text{SO}_4$ . The coloration efficiency and rates were found to depend on the amounts of added  $\text{V}_2\text{O}_5$  or  $\text{V}_2\text{O}_3$ . For example, small amounts of  $\text{V}_2\text{O}_3$  caused the films to color less deeply upon application of a voltage, but response time was faster as compared to  $\text{WO}_3$ . As the amount of  $\text{V}_2\text{O}_3$  was increased, the depth of coloration could be increased with larger voltages and the films exhibited much longer open circuit lifetimes.

These preliminary studies indicate that mixtures of  $\text{V}_2\text{O}_5$ - $\text{WO}_3$  and  $\text{V}_2\text{O}_3$ - $\text{WO}_3$  have good potential for forming EC films with high efficiency, fast coloration speed, and long lifetimes. The possibility exists of varying the energy of maximum photon absorption, and as a result changing the color of the film. A small number of experiments with co-evaporation of  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$  indicates that electrochromism also occurs in this system. The EC color was deep blue.

Metal tungstates. Powders of Ca, Sr, Ba, Ce, Rb, Na, Bi, Mg, Co, Mn, and Ni tungstates were purchased from Cerac, Inc. The ability to electrically color these powders was tested by settling them onto a glass substrate, covering with dilute  $\text{H}_2\text{SO}_4$ , and touching with an In wire.<sup>3</sup> In all instances except Mn and Ni tungstates, a blue coloration was induced. Although no dramatic color changes (e.g. red vs. blue) were observed, the blue colors ranged from light blue to black.

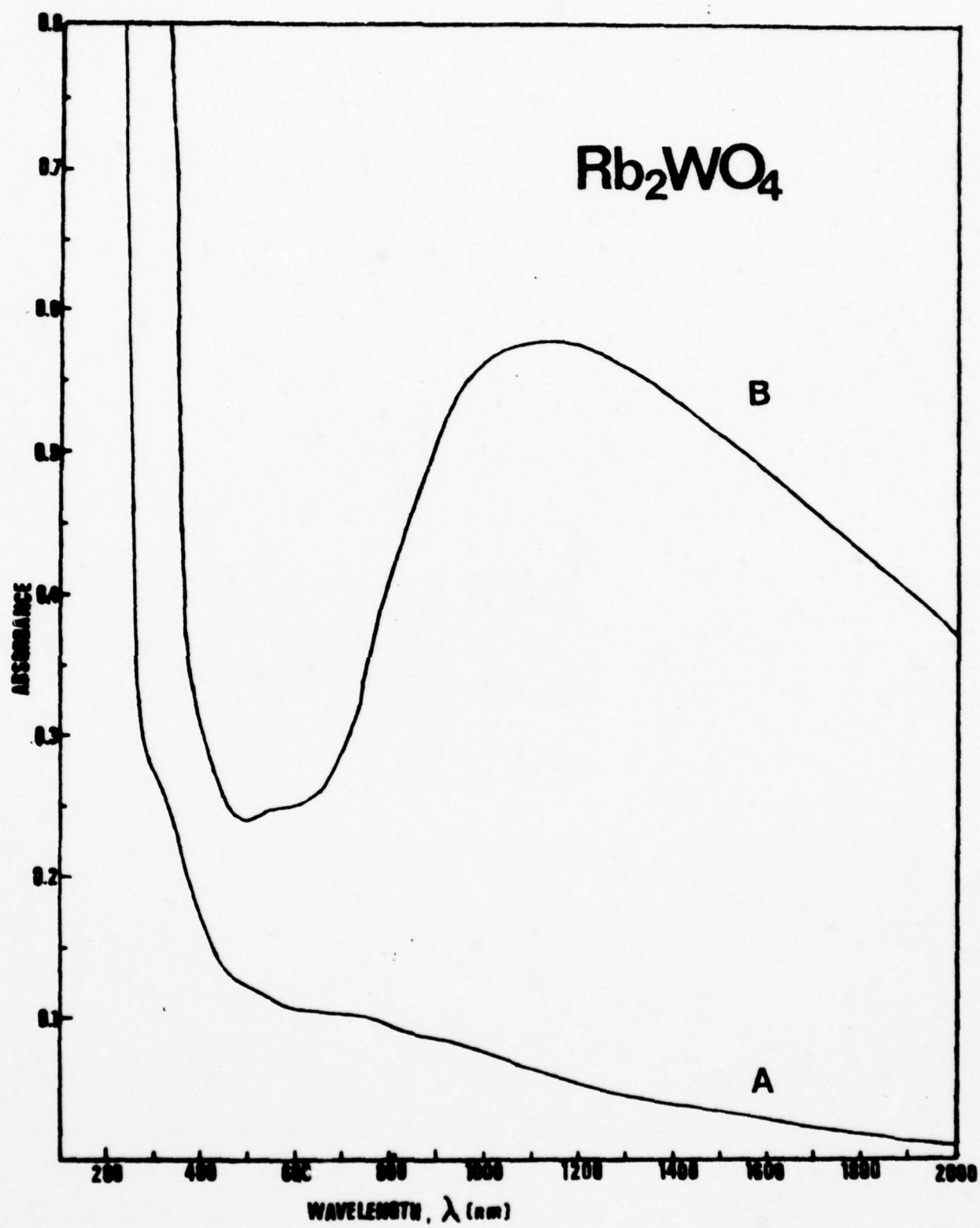
The commercial tungstate powders of Na, Rb, Ba, and Sr were vapor deposited onto glass plates with a conducting tin oxide layer. Coloration in the  $\text{BaWO}_4$  and  $\text{SrWO}_4$  could be achieved with an  $\text{H}_2\text{SO}_4$  electrolyte and either an In wire or a potential between the tin oxide and a counter electrode. The color was blue and the color depth was not equivalent to that of settled powders. The coloration could be bleached by application of a potential or of  $\text{H}_2\text{O}_2$  to the surface. However, very few samples would color again after such a bleaching treatment.

The  $\text{Rb}_2\text{WO}_4$  films turned blue immediately upon application of the acid, without the application of an electric potential (Fig. 5). The film could be erased with  $\text{H}_2\text{O}_2$  but not with an applied potential. The  $\text{Na}_2\text{WO}_4$  was blue in the as-deposited condition. The intensity of coloration could be increased somewhat by the application of a potential but the films could not be erased electrically. Based upon data by Sakka,<sup>5</sup> we have conducted a number of experiments where  $\text{Bi}_2\text{O}_3$  was added to  $\text{BaWO}_4$ . However our procedures only resulted in a blue electrochromic state in these materials (rather than a red coloration). The methods of production were varied to attempt to reproduce Sakka's results, but to no avail.



Figure 5. Absorbance spectra of  $\text{RB}_2\text{WO}_4$  film (A) as-deposited and (B) after coloration with 1 N  $\text{H}_2\text{SO}_4$ .





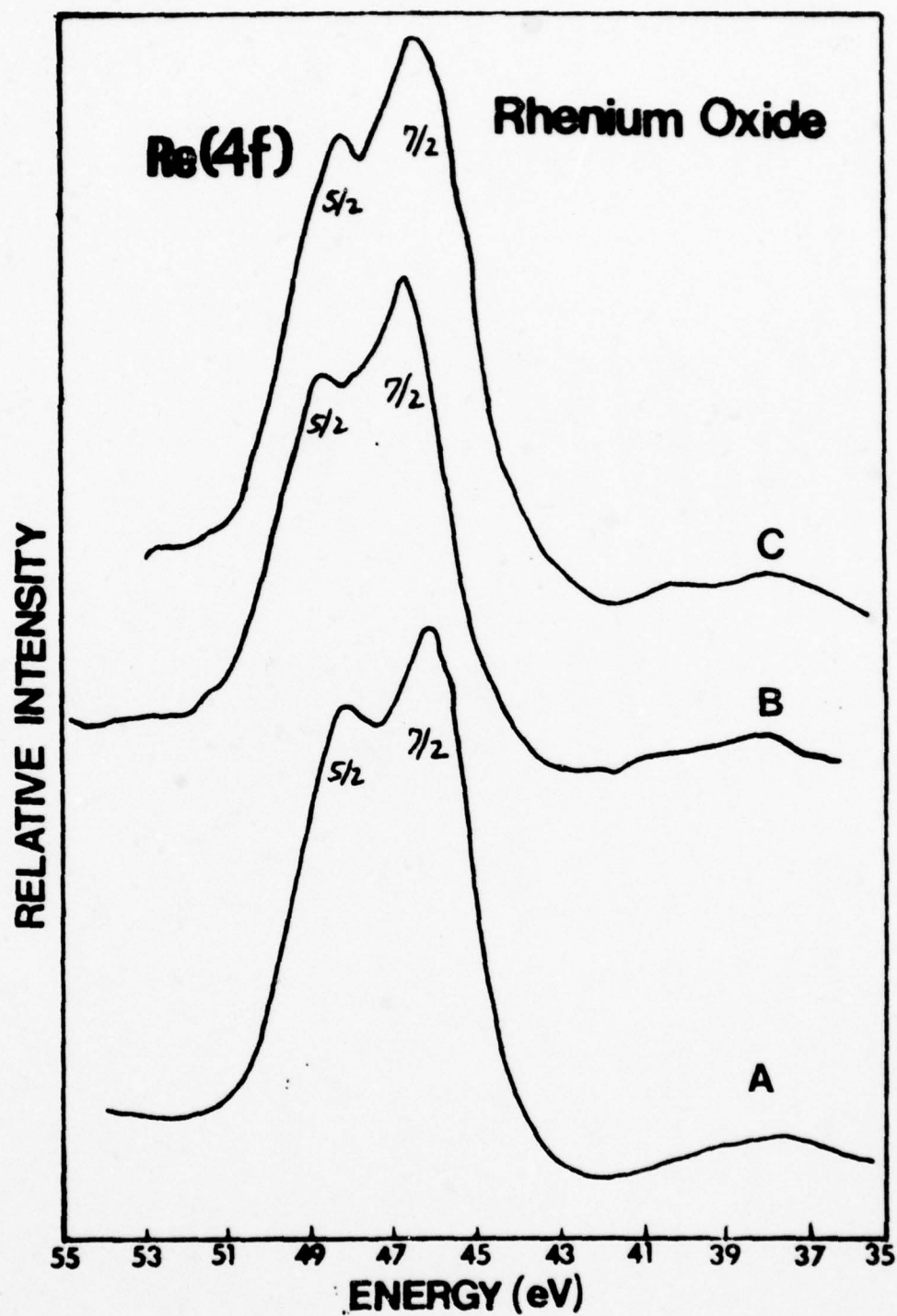


Figure 6. ESCA Re 4f core level spectra from (A)  $\text{Re}_2\text{O}_7$  powder and from films vapor deposited from powders of (B)  $\text{ReO}_3$  and (C)  $\text{ReO}_2$ .

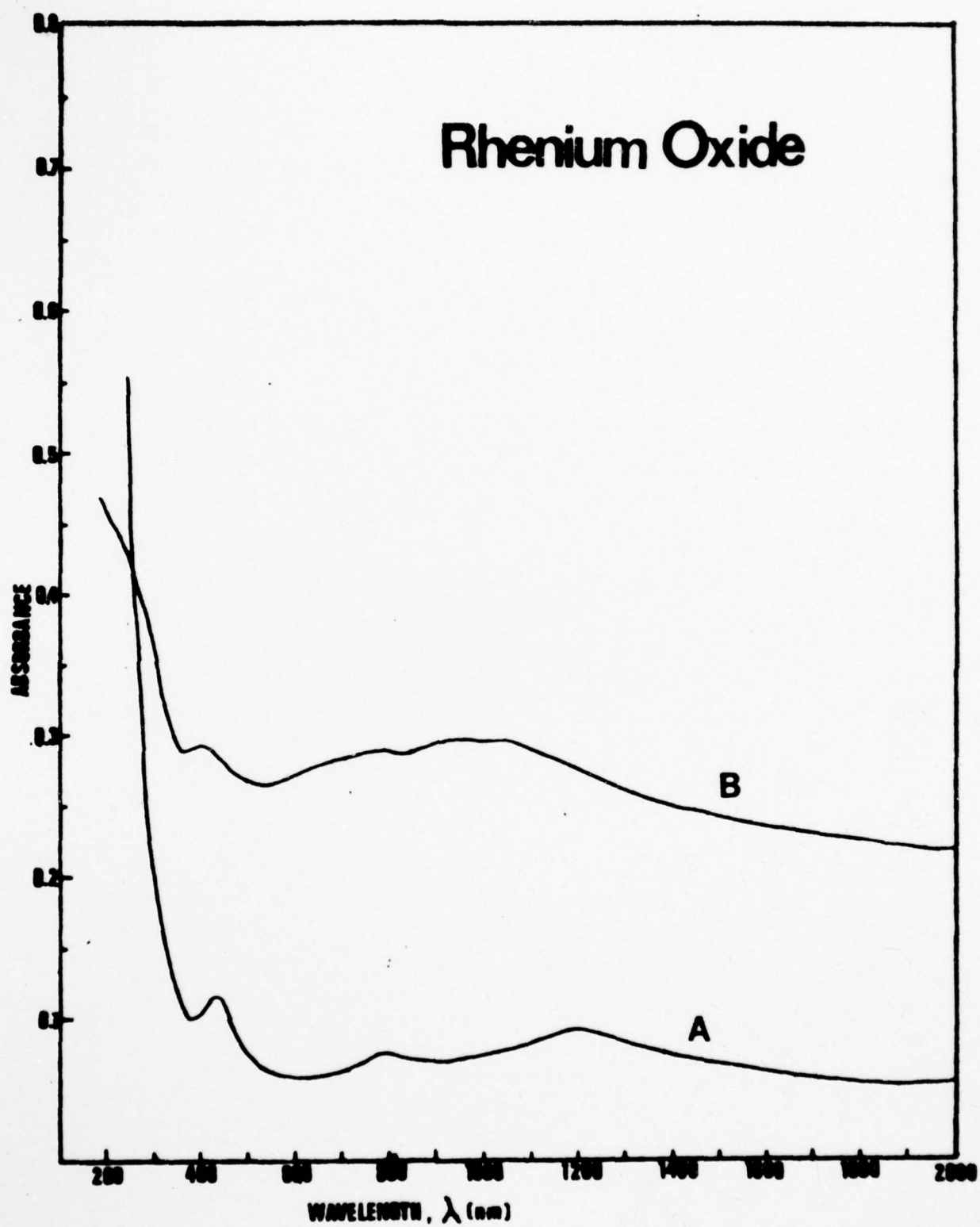
## (2) Studies of rhenium oxide

Thin films of rhenium oxide were thermally evaporated and deposited on NESA glass and quartz from powders of  $\text{ReO}_2$  and  $\text{ReO}_3$ . The films had the physical characteristics reported for  $\text{Re}_2\text{O}_7$ , i.e. they were hygroscopic and yellow in color. ESCA data indicate that films made from either  $\text{ReO}_2$  or  $\text{ReO}_3$  powder had the same electronic structure. Data in Fig. 6 show that the Re 4f photoelectron peaks from  $\text{Re}_2\text{O}_7$  powder and from films deposited from  $\text{ReO}_2$  and  $\text{ReO}_3$  powders respectively are very similar. The Re peaks in  $\text{Re}_2\text{O}_7$  are shifted to a higher binding energy ( $4f^{7/2}$  binding energy of 46.2 eV) than those reported for  $\text{ReO}_3$  ( $4f^{7/2}$  binding energy of 43.2 eV),<sup>13</sup> which is consistent with the higher valence state ( $\text{Re}^{7+}$ ). The formation of  $\text{Re}_2\text{O}_7$  as a decomposition product obtained by heating  $\text{ReO}_2$  or  $\text{ReO}_3$  in vacuum is also consistent with the findings reported by Druce.<sup>14</sup>

As reported earlier, films of  $\text{Re}_2\text{O}_7$  exhibited a reversible EC effect when touched with an indium wire in the presence of 1 N  $\text{H}_2\text{SO}_4$ , or when a small potential was applied across the film using the acid electrolyte.<sup>15</sup> The film changed from transparent yellow to deep blue. Figure 7 shows the absorption spectra for a  $\text{Re}_2\text{O}_7$  film before and after EC coloration. The blue coloration develops because of an absorption band with maxima at 700 nm (red) and 1100 nm (near infrared) and a minimum at 500 nm (blue). It is noted that only a portion of the irradiated area was colored, so that the spectrum of the colored film possesses some features of the original  $\text{Re}_2\text{O}_7$ . Colored areas of  $\text{Re}_2\text{O}_7$  sufficiently large for optical absorption measurements are quite difficult to obtain

Figure 7. Absorbance spectra for  $\text{Re}_2\text{O}_7$  (A) as-deposited and (B) after electrochromic coloration.





electrochromically. The hygroscopic nature of the films results in a break-up and separation from the substrate in the area beneath the acid.

Because of its hygroscopicity, techniques to passivate the  $\text{Re}_2\text{O}_7$  toward  $\text{H}_2\text{O}$  adsorption were studied.  $\text{SiO}$  layers  $\sim 400$  nm thick effectively passivated the  $\text{Re}_2\text{O}_7$  film toward absorption of  $\text{H}_2\text{O}$  from the atmosphere, but they were not sufficient to prevent the acid electrolyte from soaking through to the  $\text{Re}_2\text{O}_7$  during coloration. The  $\text{Re}_2\text{O}_7$  films could be EC colored with these  $\text{SiO}$  films in place.

Besides exhibiting an EC effect,  $\text{Re}_2\text{O}_7$  also was found to exhibit a thermochromic (TC) effect. Heating the as-deposited films to  $100^\circ\text{C}$  to  $150^\circ\text{C}$  for times as short as 30 sec. resulted in coloration. Figures 8-10 show progressive changes in the optical absorption spectra as the time of heating at  $150^\circ\text{C}$  was increased. The heated films appeared blue or greenish-blue in transmission and red in reflection. After 3 min. of heating the absorption spectrum showed a broad band with a maximum at  $\sim 1400$  nm and an absorption minimum at 500 nm (blue). The colored state is retained upon cooling to room temperature but can be removed by bleaching with  $\text{H}_2\text{O}_2$ . Similar effects were found during heating of  $\text{Re}_2\text{O}_7$  powders.

The composition and structure of the  $\text{Re}_2\text{O}_7$  films were studied to identify the origin of the TC effect. X-ray (Fig. 11) and electron diffraction data indicated that the as-deposited films were amorphous. Upon heating in air or vacuum, both x-ray (Fig. 11) and electron diffraction data indicated that crystallites of  $\text{ReO}_3$  were formed. ESCA results were

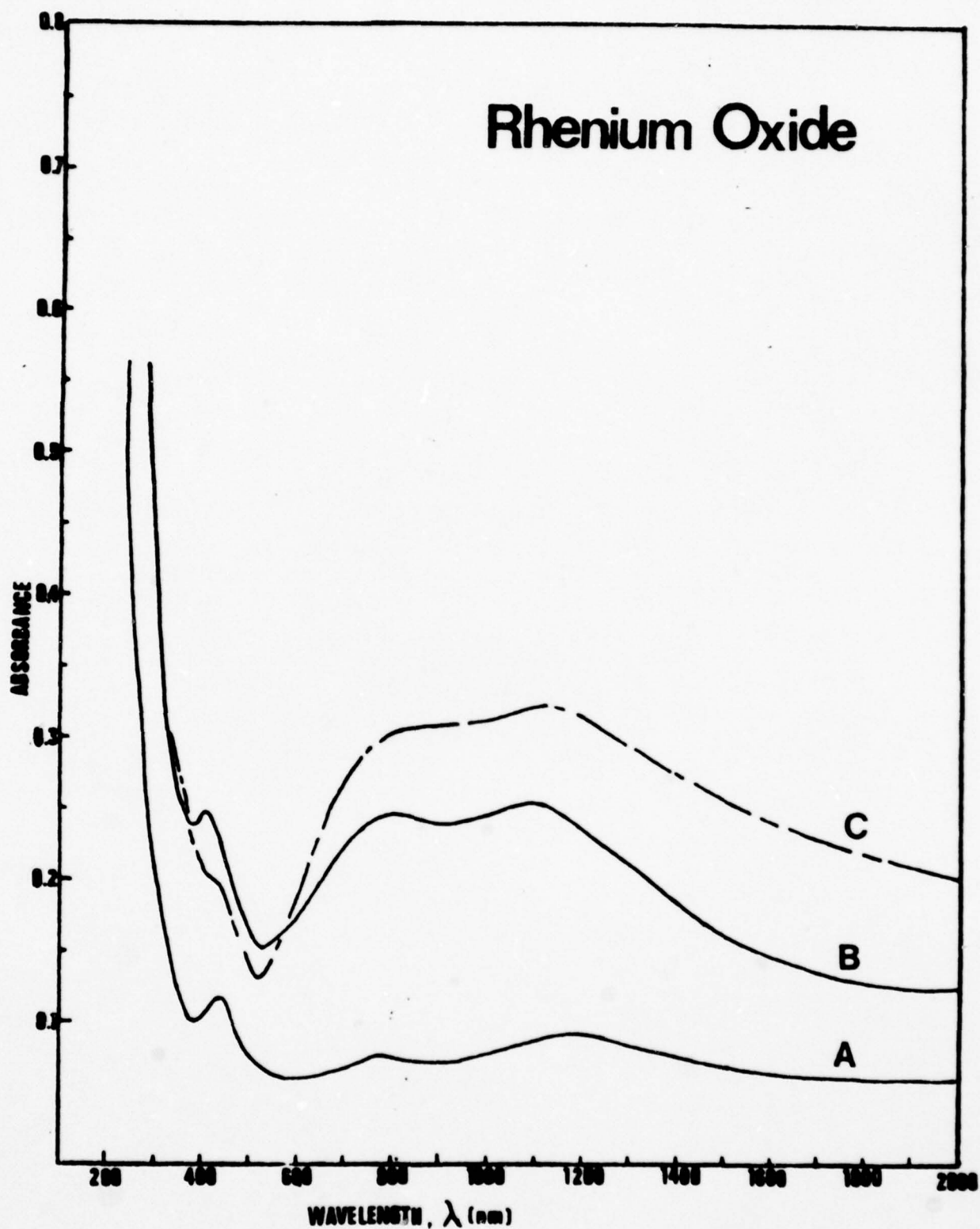


Figure 8. Absorbance spectra of  $\text{Re}_2\text{O}_7$  (A) as-deposited and after heating in air at  $150^\circ\text{C}$  for (B) 0.5 min. and (C) 1 min.

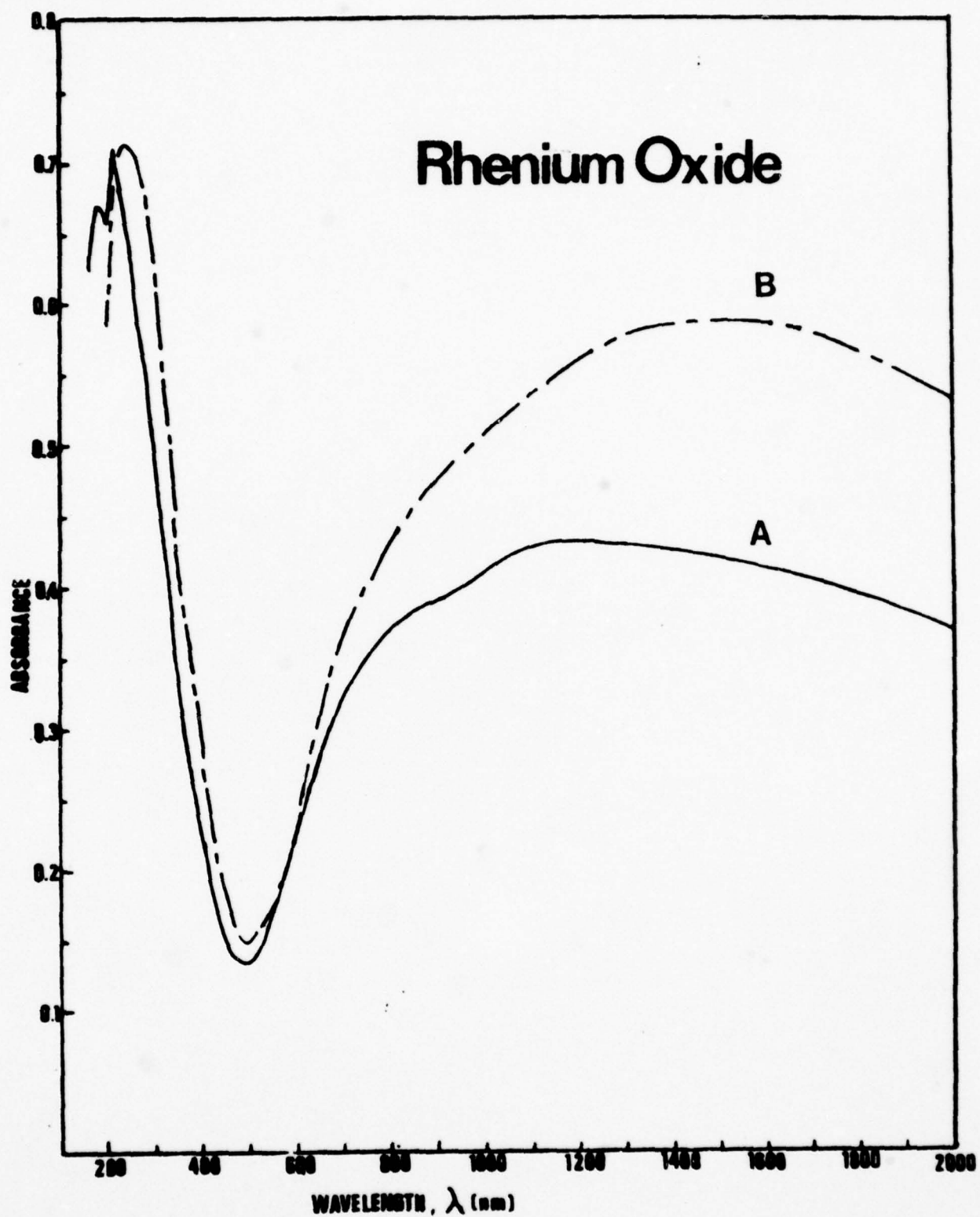


Figure 9. Absorbance spectra of  $\text{Re}_2\text{O}_7$  after heating in air at  $150^\circ\text{C}$  for (A) 1.5 min. and (B) 2 min.



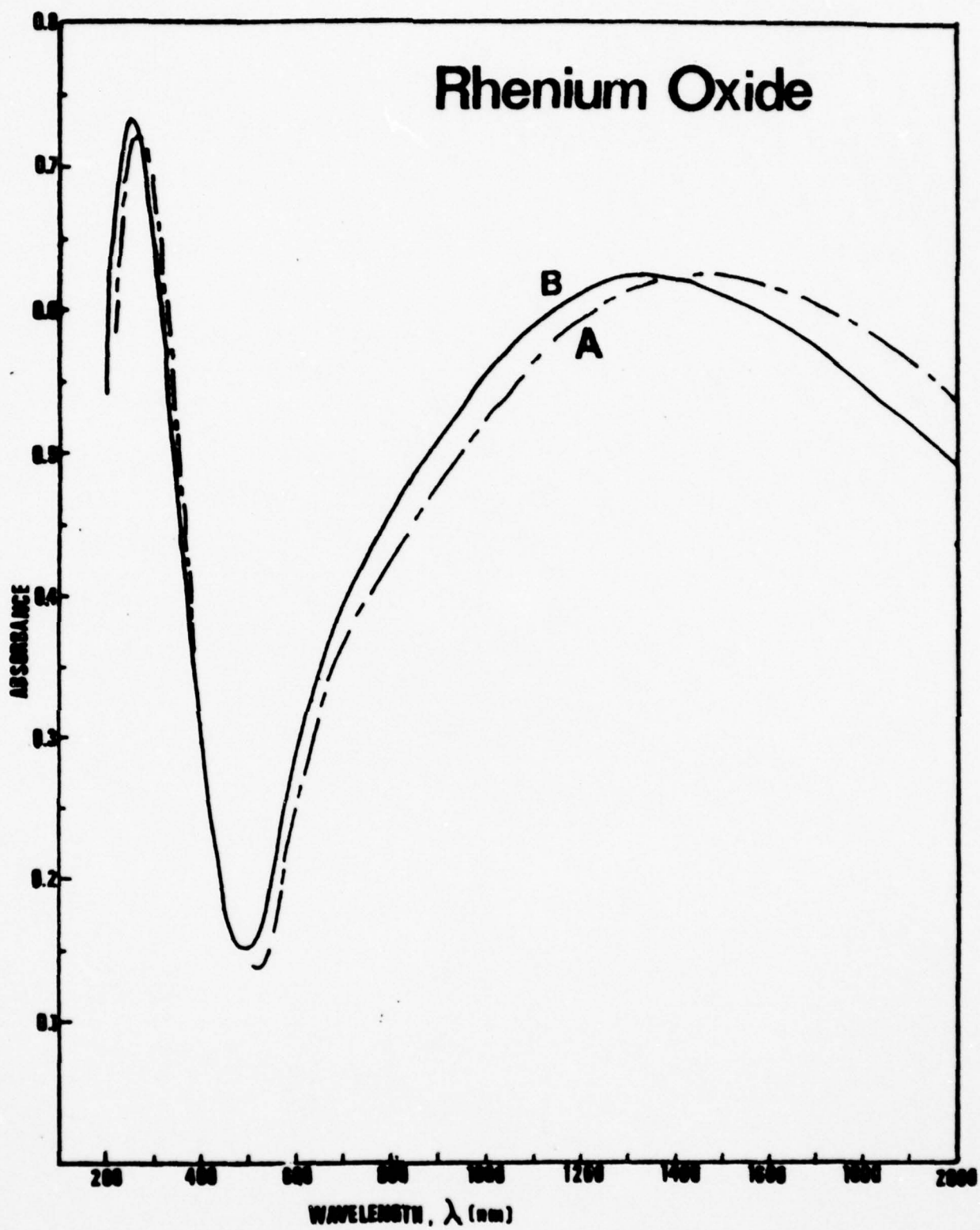


Figure 10. Absorbance spectra of  $\text{Re}_2\text{O}_7$  after heating in air at  $150^\circ\text{C}$  for (A) 3 min. and (B) 11 min.

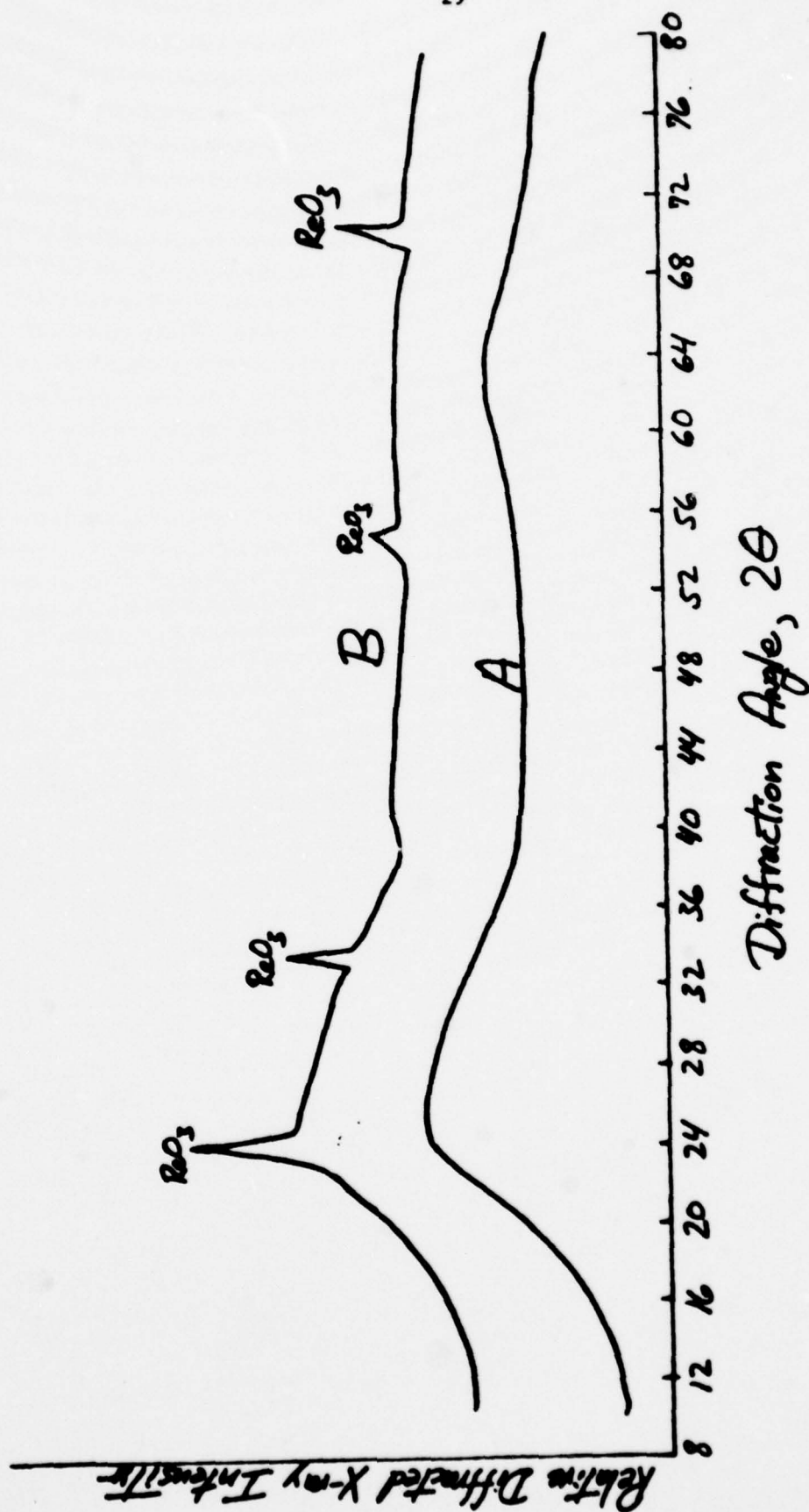


Figure 11. X-ray diffraction spectra of  $\text{Re}_2\text{O}_7$  film on soda-silicate glass (A) as deposited and (B) after heat treatment at  $150^\circ\text{C}$  for 2 min.

consistent with this finding. Figure 12 shows that the Re 4f spectrum of a TC-colored film contains features representing a combination of the features from both  $\text{ReO}_3$  and  $\text{Re}_2\text{O}_7$ . Thus the TC effects appear to be a result of a crystalline change in the thin films. The similarity of the TC and EC absorption spectra suggest that the origin of the EC effect may be of a similar nature.

(3) Electrochromic rate-controlling mechanisms in liquid electrolyte devices<sup>16</sup>

We have found that the application of a thin semi-transparent conducting layer to the  $\text{WO}_3$  surface very markedly increases the rate of coloration that may be achieved.<sup>1</sup> The optical absorption of the conducting film was typically 5-10%. In addition, it has been found that the application of a small voltage to the conducting film, imposed in addition to the potential applied between the  $\text{SnO}_2$  film and electrolyte, gives rise to a considerable increase in rate of coloration and bleaching.

The electrochemical cell in which the  $\text{WO}_3$  film is placed in contact with 1 N  $\text{H}_2\text{SO}_4$  has been shown in Fig. 1. Normally when the conducting layer was present, voltages were simultaneously applied to the  $\text{SnO}_2$  layer, to the thin conducting surface layer, and to the counter electrode.

Figure 13 shows the change in optical transmission at 900 nm for a coloration and bleaching sequence obtained with 1.5 V applied between the  $\text{SnO}_2$  and counter electrode. Curves a and b refer to a  $\text{WO}_3$  film without and with a thin conducting surface layer respectively. Coloration proceeds rapidly when the  $\text{SnO}_2$  layer is made negative relative to the electrolyte. Reversing the voltage gives rise to bleaching. Figure 13

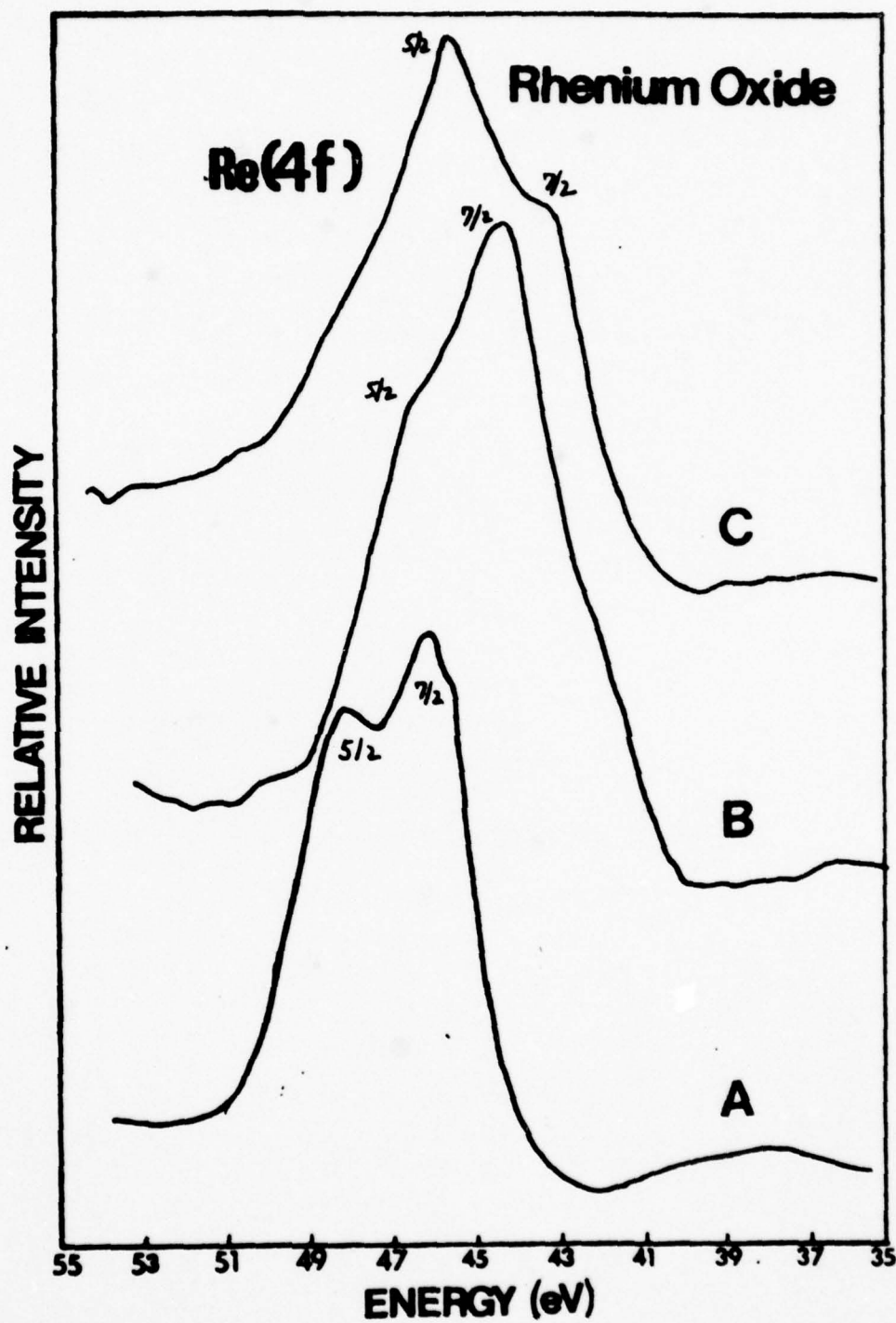
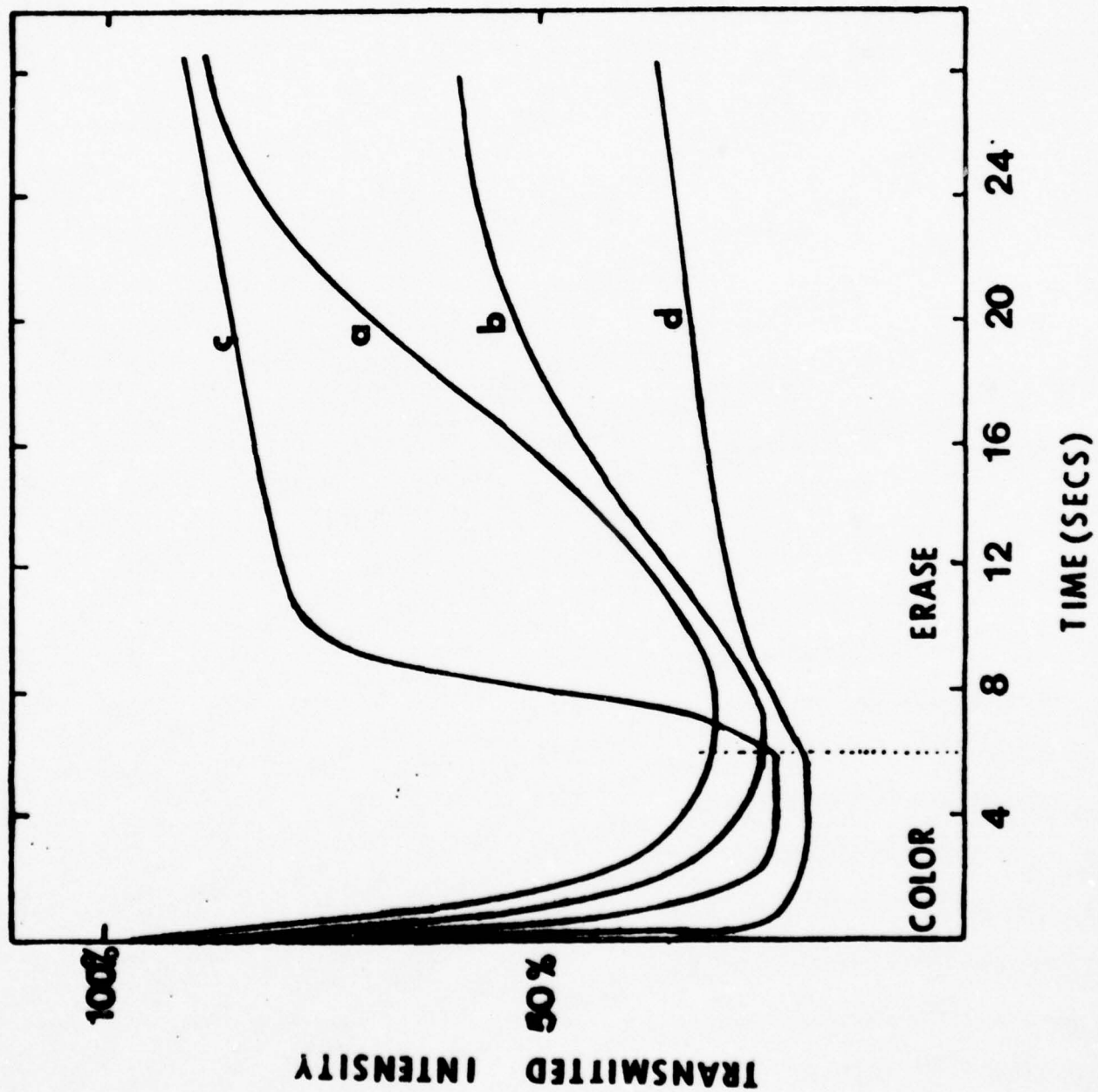


Figure 12. ESCA Re 4f core level spectra for (A)  $\text{Re}_2\text{O}_7$  powder, (B)  $\text{ReO}_3$  powder, and (C) a film vapor deposited from  $\text{ReO}_2$  and colored by heating in air at  $150^\circ\text{C}$  for 0.5 min.



Figure 13. Change in optical transmission at 900 nm during a coloration and bleaching sequence. Curves (a) and (b) refer to  $\text{WO}_3$  without and with a conducting overlayer, respectively. Curves (c) and (d) refer to  $\text{WO}_3$  with +0.5 and -0.5 volts on the conducting surface layer with respect to the  $\text{SnO}_2$  layer, in addition to 1.5 V between the  $\text{SnO}_2$  and counter electrode.



shows that the presence of the conducting layer gave rise to a significant increase in the rate of coloration. Application of either +0.5 volts or -0.5 volts to the conducting layer electrode produced further increases in the rate of coloration, as shown in curves c and d. However, the application of +0.5 volts to the conducting layer gave rise to an increase in bleaching rate while a voltage of -0.5 V led to a large decrease in bleaching rate. With -0.5 V during coloration and +0.5 V during bleaching, very fast switching was observed (i.e. curves d and c were combined).

Coloration or bleaching could not be obtained by applying a potential between the  $\text{SnO}_2$  layer and the gold layer when the connection between the  $\text{SnO}_2$  layer and the counter electrode was removed. However, application of a voltage between the conducting layer and the counter electrode with the  $\text{SnO}_2$  electrode disconnected was found to lead to coloration. Apparently electrons may enter the  $\text{WO}_3$  from the conducting film to maintain charge balance when the protons enter the  $\text{WO}_3$  film. Reversing the voltage however did not lead to substantial bleaching when the  $\text{SnO}_2$  electrode was disconnected. The effect of the conducting film became much less marked as the film thickness was increased, probably because the porosity decreased and proton transport to the  $\text{WO}_3$  film was blocked.

These results become understandable when it is realized that when the gold layer is not connected to an external voltage source, it attained a potential of approximately 1.2 volts relative to the  $\text{SnO}_2$  film during coloration. While this affects the rate of C/B, it cannot explain the kinetics of the cells without the incorporation of a term accounting for resistance in the  $\text{WO}_3$  and/or  $\text{SnO}_2$  layer. In fact current/voltage measurements

indicate that this resistance has values of 100-200  $\Omega$  in cells without a conducting layer. With a conducting layer on the surface of  $\text{WO}_3$ , the resistance was lower. A third consideration in writing equations to describe the kinetics of our electrochemical cell is that the equilibrium cell potential is a function of the composition of the  $\text{WO}_3$  layer. As protons are injected into the film, the equilibrium potential shifts<sup>17</sup> and this will affect the resulting kinetics. With these considerations we write the overpotential,  $\eta$ , as

$$\eta = E - E_e + j_p R_\Omega \quad (1)$$

where  $E$  is the potential applied,  $E_e$  is the equilibrium potential which varies with composition,  $j_p$  is the current, and  $R$  is the  $\text{WO}_3/\text{SnO}_2$  resistance. Using the Butler-Volmer equation,<sup>18</sup>

$$j_p = j_o [\exp[\frac{(1-\alpha)e\eta}{kT}] - \exp[-\frac{\alpha e\eta}{kT}]] \quad (2)$$

where  $j_o$  is the exchange current density (assumed constant),  $\alpha$  is the barrier symmetry factor,  $k$  = Boltzmann's constant,  $T$  is temperature, and  $e$  is the electronic charge. We can substitute  $\eta$  and reduce Eq. (2) to

$$j_p = \frac{(E-E_e) [e/kt(E-E_e) + 1]}{P\sqrt{t} - R_\Omega [e/kt(E-E_e)+1]} \quad (3)$$

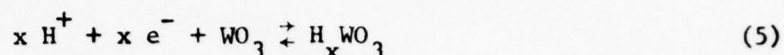
where

$$P = -\frac{RT\pi^{1/2}}{2F^2 c^* AD^{1/2}} \quad (4)$$

and  $R$  is the gas constant,  $F$  is the Helmholtz constant,  $c^*$  is the bulk



concentration, A is the area of the colored portion, D is the proton diffusion coefficient, and x is the number of electrons in the reaction



Equation (3) shows that if the resistance is high, the current is dominated by the term containing  $R_\Omega$  and is independent of time. However, if the Helmholtz layer dominates, the kinetics are dependent upon  $t^{-1/2}$ . A plot of current versus  $t^{-1/2}$  from the present cell is shown in Fig. 14. The current initially tends to be independent of time indicating resistance control. However at longer times, the kinetics become diffusion controlled and the current shows the  $t^{-1/2}$  dependence.

This conclusion is supported by cyclic voltammetry measurements of which a typical example is shown in Fig. 15. In this technique the potential between the  $\text{SnO}_2$  and Pt counter electrode was cyclically swept at various speeds,  $v$ (volts/sec). The data indicate that the peak current for bleaching obeys the  $v^{1/2}$  law for both  $\text{SnO}_2/\text{WO}_3$  and  $\text{SnO}_2/\text{WO}_3/\text{conducting layer}$  cells. This  $v^{1/2}$  dependence has previously been ascribed to diffusion control across the Helmholtz layer,<sup>19</sup> and is consistent with the conclusion that the Helmholtz layer may limit the rate of coloration (after a finite time) in EC devices. As might be expected based upon this hypothesis, the rate of coloration (i.e. the peak current increase) was higher for  $\text{SnO}_2/\text{WO}_3/\text{conducting layer}$  cells versus  $\text{SnO}_2/\text{WO}_3$  cells as shown in Fig. 15. In addition, data in Fig. 15 show that the coloration rate increased even further when the conducting layer was electrically shorted to the  $\text{SnO}_2$  layer or when the conducting layer was at a negative

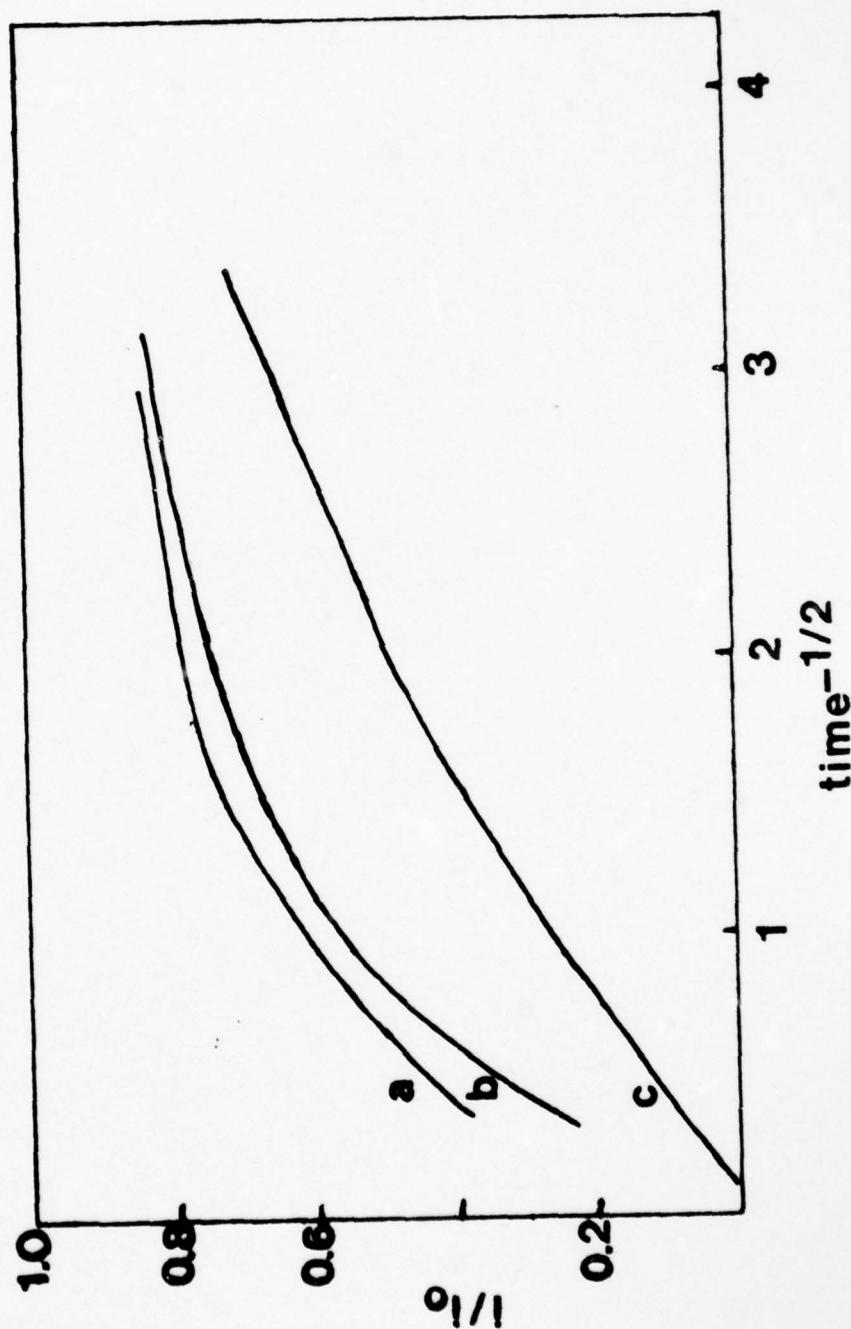
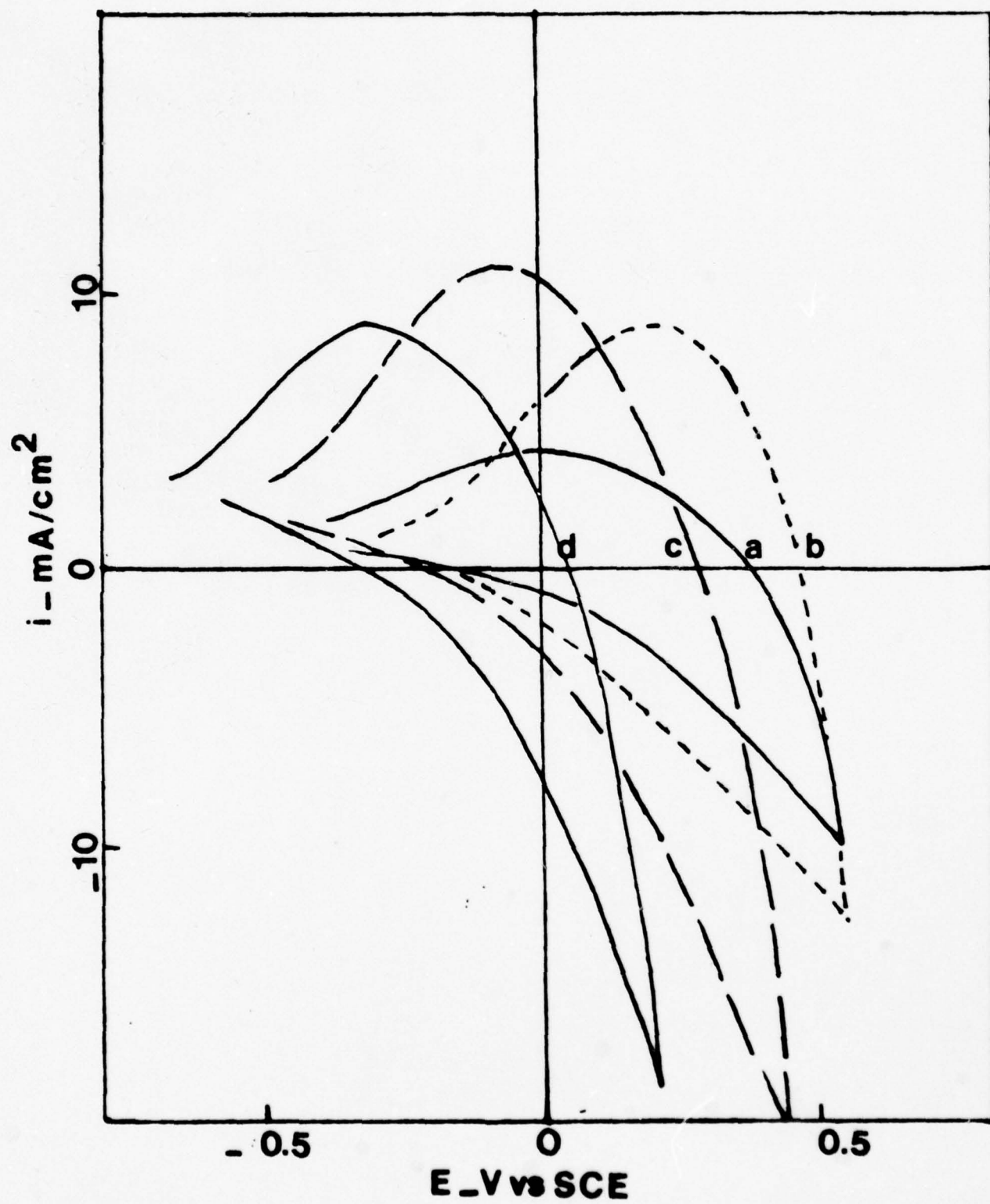


Figure 14. Current ( $I$ ) changes with time during coloration normalized to the initial current ( $I_0$ ) versus the inverse of the square root of time. Curves a, b, and c refer to +0.6, +0.4, and +0.1 volts respectively applied to  $\text{SnO}_2$  and referenced to the calomel electrode.

Figure 15. Cyclic voltametry curves of current versus potentiostatic voltage reference to the calomel electrode. Curves a, b, c, and d refer to  $\text{WO}_3$ ,  $\text{WO}_3$  with an electrically floating conducting layer,  $\text{WO}_3$  with the conducting layer shorted to the  $\text{SnO}_2$  layer, and with a potential of  $-0.1$  volts applied to the conducting layer, respectively.





potential with respect to the  $\text{SnO}_2$ .

Initially the coloration of  $\text{WO}_3$  is not controlled by the Helmholtz layer and we have modelled this effect by adding a resistance term to the overpotential expression. However this effect could originate from resistance to injecting protons into the  $\text{WO}_3$  films. To study this effect we have measured the flat band voltage for the devices in a photoelectrolysis experiment. A potentiostatic voltage was applied to the  $\text{SnO}_2$  with respect to the Pt counter electrode and referenced to the calomel electrode. A mercury lamp was used to flood the cell with a spectrum of photons with good intensity at  $\sim 300$  nm. A typical variation of photo current with voltage is shown in Fig. 16. The data show that the flat band voltages (the voltage necessary to compensate band bending at the surface) vary with the pH of the solution. The flat band voltage decreases as the pH increases and the slope is  $0.059$  mV/pH, which is similar to data reported by Bulter *et al.*<sup>20</sup> The  $\text{WO}_3$ /conducting layer cells were found to have a lower flat band voltage in  $0.5$  N  $\text{H}_2\text{SO}_4$  electrolyte ( $0.25$  V) as compared to  $\text{WO}_3$  cells ( $0.48$  V), but in either case the flat band voltage decreased as pH increased. Data in Fig. 15 show that hydrogen was evolved at lower voltages with the conducting layer on the  $\text{WO}_3$ , and this probably results from the effects of the conducting layer upon the flat band voltage. There is also evidence that the conducting layer increased the pH of the surface, probably by increasing the concentration of adsorbed protons on the surface.

Beyond investigating the rate of coloration versus sweep rate, the cyclic voltamogram in Fig. 17 demonstrates that  $\text{H}_2$  is evolved in the

Figure 16. The variation of photocurrent with voltage applied to  $\text{SnO}_2$  and referenced to the calomel electrode for (a)  $\text{WO}_3$  on  $\text{SnO}_2$  coated glass and for (b)  $\text{WO}_3$  with a conducting layer in 0.5 N  $\text{H}_2\text{SO}_4$  electrolyte.

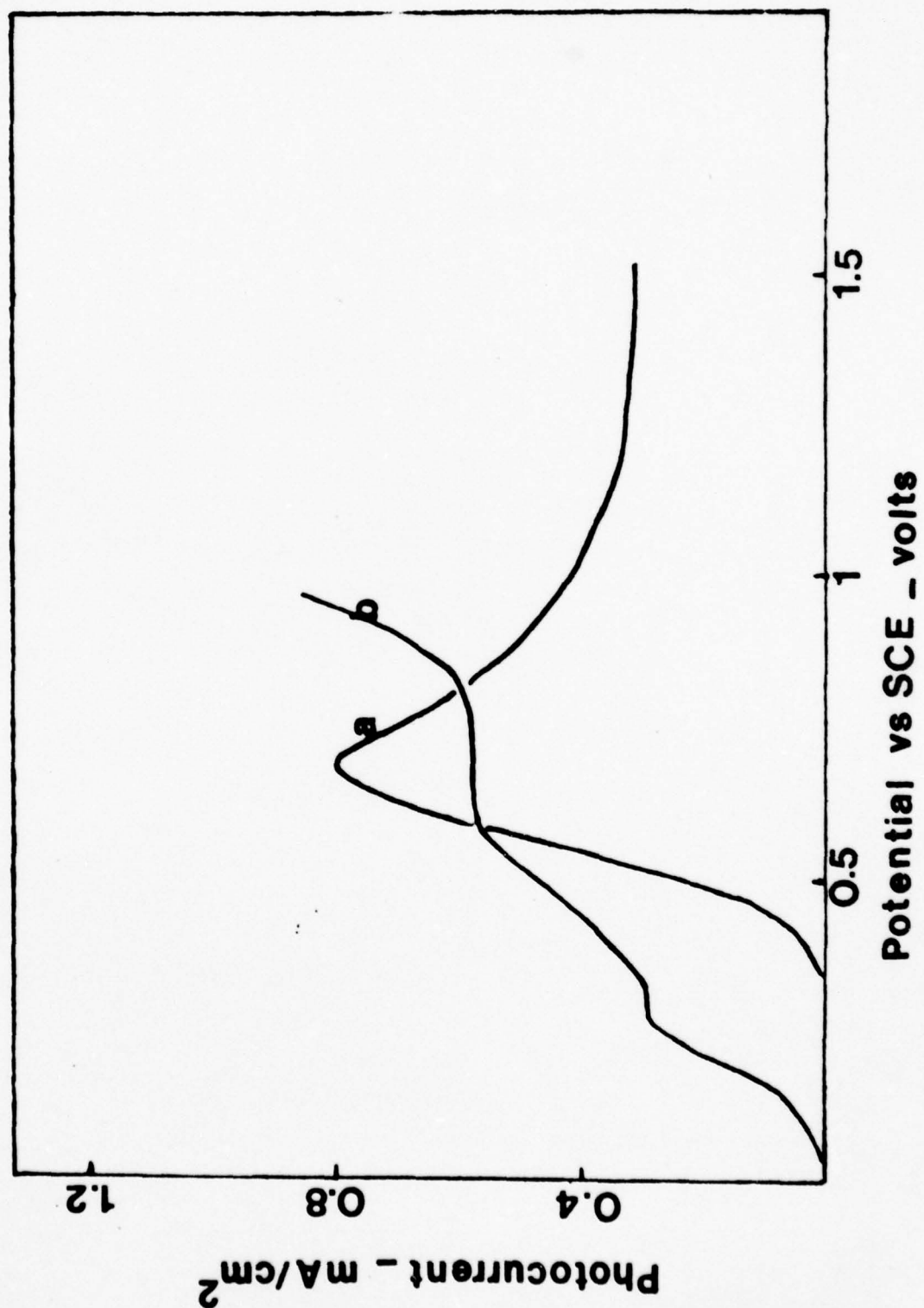
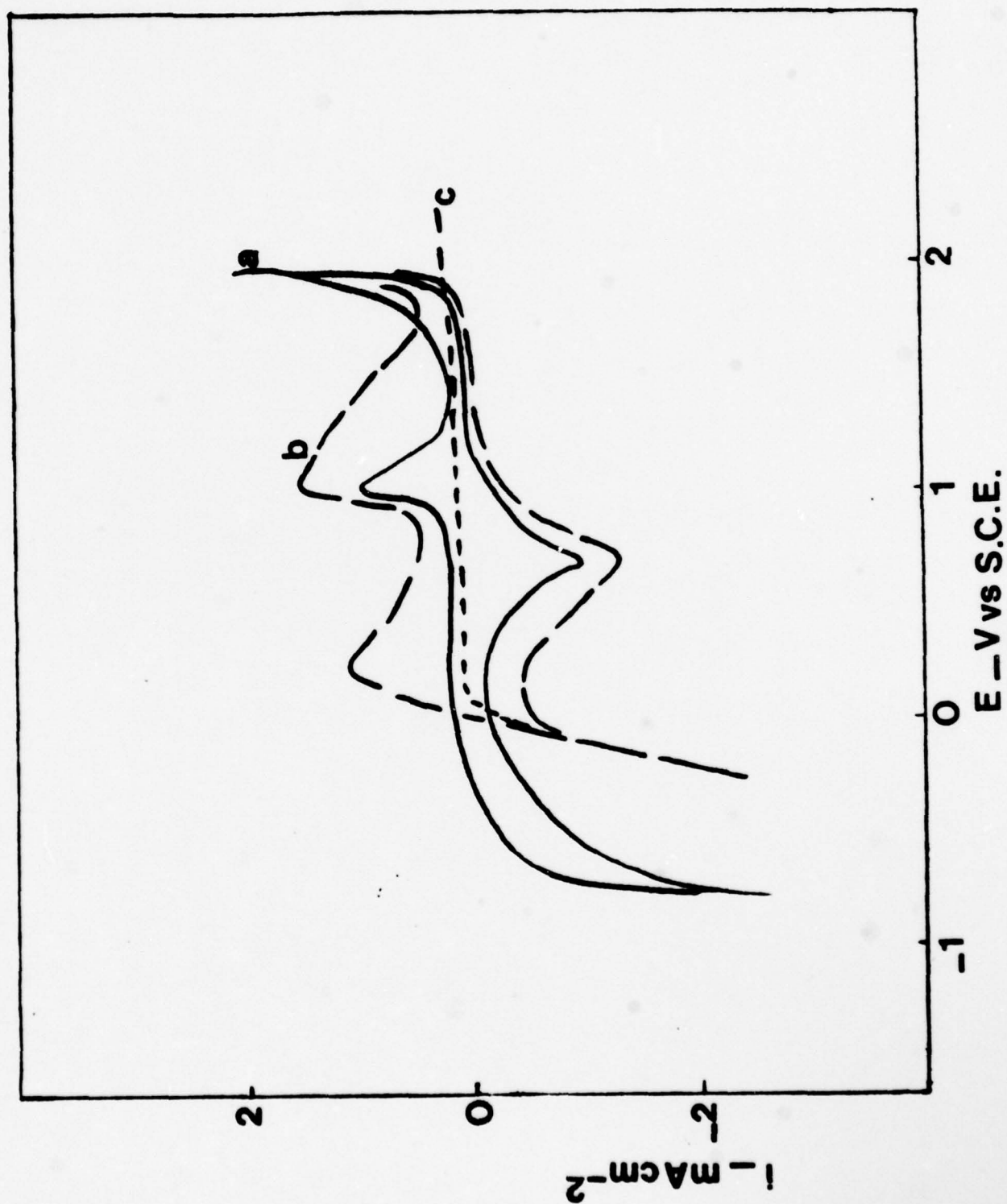


Figure 17. Cyclic voltammetry curves for (a) a conducting layer on glass, (b) a nonporous conducting layer on  $WO_3$ , and (c) a porous conducting layer on  $WO_3$ .





cathodic limit, and the current peaks at +1.1 and +0.8 volts represent oxidation and reduction, respectively, of the conducting layer. To study this effect further, conducting layers were deposited on glass substrates as well as on  $\text{WO}_3$  on  $\text{SnO}_2$ . The behavior of each of these types of samples was studied in electrochemical cells, as well as in composite cells where both substrates were incorporated simultaneously. The extent of oxidation and reduction of the conducting layer was substantial and similar on glass substrates and  $\text{WO}_3$  substrates when the layer was continuous and nonporous. However upon cycling a few times between the anodic and cathodic limits, the conducting layer became porous, and the hydrogen evolution potential increased to a value between that for a uniform, nonporous conducting layer and for  $\text{WO}_3$  surfaces. In this condition the conducting layer appeared resistant to oxidation and reduction as shown in Fig. 16. Some evidence for corrosion of the  $\text{WO}_3$  itself was found, and the extent depended upon the history of the sample. The voltages at which  $\text{WO}_3$  corrosion was significant were larger for films which had been heat treated for 60 min. at  $250^\circ\text{C}$ , however the depth of coloration was lower in these samples. As-deposited  $\text{WO}_3$  displayed larger absorption coefficients, but the corrosion occurred at lower applied voltages.

The effects of the conducting layer porosity upon hydrogen evolution is similar in many respects to the results of Harris *et al.*<sup>21</sup> for gold layers on GaP. They also found less corrosion of the overlayer for a porous film, yet their overlayer displayed blisters after ~100 cathodic-anodic cycles. Harris *et al.* controlled blistering by producing porosity

during deposition of the overlayer and by limiting the voltage extremes to below those at which gas was evolved. Similar characteristics in our films have been reported above.

Because of the patent being applied for,<sup>1</sup> the specific nature of the conducting layer has not been discussed in this report. A number of different materials were studied, and an optimized material and deposition technique has been selected. The University is currently discussing patent rights with various commercial companies.

#### (4) solid-state electrochromic devices

Solid-state cells were made using SiO and a proprietary solid state electrolyte (PSSE) as the source of positive ions. In the WO<sub>3</sub>-SiO cell, the injected ions are H<sup>+</sup> ions present in the SiO and WO<sub>3</sub> due to absorbed water vapor.<sup>22</sup> The WO<sub>3</sub> could be colored and bleached as usual by application of a voltage. The rate of coloration was found to be much slower than that using an acid electrolyte, i.e. approximately 10 sec. being required to reach 10% absorption.

The PSSE electrolyte is a rapid proton conductor whose conductivity at room temperature has been found to be higher than that of  $\beta$ -Al<sub>2</sub>O<sub>3</sub>. PSSE was prepared by pressing it into pellets which were pressed against NESA glass with a deposited WO<sub>3</sub> film. The opposite side of the PSSE was either coated with Ag paste or pressed against another NESA glass plate. For better adhesion and uniform surface contact to WO<sub>3</sub> films, the pressed pellets were coated with a thin layer of PSSE paste. The paste was made using less than 1% by volume of 1 N H<sub>2</sub>SO<sub>4</sub>. This structure was dried in water-rich atmospheres at 50-80°C for 1/2 h. The speed of coloration



and bleaching with this electrolyte was comparable to that of dilute  $\text{H}_2\text{SO}_4$  as an electrolyte. As shown in Table 1, this method results in a reflectivity difference of 36% after 0.7 sec. at 5 mA. Here reflectivity difference is defined as  $(R_1 - R)/R_1 \times 100\%$ , where  $R_1$  and  $R$  are the initial and instantaneous reflected light intensities. However, high applied voltages were required to reach the same degree of coloration as compared to  $\text{H}_2\text{SO}_4$ , due to resistance of the 1 mm thick electrolyte. This resistance can be decreased by using more dense and thinner electrolyte pellets.

PSEE was successfully applied as a paste, in addition to the above technique. In one method, PSSE paste was made using a binder, e.g. potassium silicate. This paste was applied to the  $\text{WO}_3$ -coated NESA glasses by a doctor-blading technique. Silver paste was used as a counter electrode. This was dried in the same manner as above. In a second procedure, pastes were made by dissolving PSSE in dilute  $\text{H}_2\text{SO}_4$ , reprecipitating with NaOH and filtering. This gave a very fine particle size. Tungsten trioxide-coated NESA glass was coated with this paste, then dried as above. Similar PSSE pastes were also used in cells as a liquid electrolyte for electrochromic coloration. In all preparation the electrochromic response time was faster than that reported by Green *et al.*<sup>23</sup> for  $\beta\text{-Al}_2\text{O}_3$  electrolytes (see Table 1).

In all devices except those with high density pellets, PSSE was opaque and colored yellow, which contrasted well with the blue electrochromic color. High density pellets developed a translucent character which would allow its use as a backlighted display. PSSE is also insoluble in water and is stable up to 80°C in atmosphere. Although lifetime data



Table 1: Electrochromic Response versus Electrolyte type and Electrolyte Treatment

Material	Treatment	Thickness of the Electrolyte	Current mA	Voltage Applied (Volts)	Reflection Contract	Response Time
1. Dilute $H_2SO_4$		-	5	0.6	36%	0.6 sec
2. PSSE Pellet Dried at 80°C		1 mm	5	15	36%	1.0 sec
Dried at 50°C		1 mm	5	5-8	36%	0.7 sec
3. PSSE Paste	With potassium silicate binder (dry)	0.5 mm	3	20	36%	5.0 sec
	Reprecipitated from	0.5 mm	4	15	36%	2.0 sec
	dilute $H_2SO_4$	1 mm	5	1-2	36%	0.7 sec
	solution					
4. $\beta-Al_2O_3$			0.3		~30%	10 sec

are very sparse, no degradation of  $WO_3$  films was observed in devices operated at low voltages. Upon coloring and opening the electrical circuit, some of the devices showed a decrease in reflectivity difference of about 5%. A 100 Å layer of SiO<sub>2</sub> deposited on the  $WO_3$  films reduced this open circuit change in reflection contrast. A patent disclosure has been filed to protect the University's rights to this discovery.

## References

1. D. B. Dove, A. R. Haranahalli, and B. J. Molnar, Patent applied for, disclosed June 6, 1977.
2. A. R. Haranahalli, P. H. Holloway, and R. E. Hummel, Patent disclosure filed October 20, 1978.
3. R. S. Crandall and B. W. Faughman, Appl. Phys. Lett. 26, 120 (1975).
4. P. H. Holloway and G. E. McGuire, Thin Solid Films 35, 3 (1978).
5. S. Sakka, J. Amer. Ceram. Soc. 52, 70 (1969).
6. S. K. Deb, Phil. Mag. 27, 801 (1973).
7. B. W. Faughman, R. S. Crandall, and P. M. Heyman, RCA Review 36, 177 (1975).
8. R. J. Colton, A. M. Gugman, and J. W. Rabalais, Acct. Chem. Res., 170 (1978); J. Appl. Phys. 49, 409 (1978).
9. H. Witzke and S. K. Deb, presented at 19th annual AIME Elect. Mat. Conf., Cornell, July 1977.
10. B. J. Molnar, A. R. Haranahalli, and D. B. Dove, J. Vac. Sci. Technol. 15, 261 (1978).
11. L. D. Bogomolova, V. N. Latukin, and N. V. Petrovykh, Soviet Physics-Doklady 12, 1046 (1968).
12. B. W. Faughman and R. S. Crandall, Appl. Phys. Lett. 31, 834 (1977).
13. M. Campagna et al., Phys. Rev. Lett. 34, 738 (1975).
14. J. G. F. Druce, Rhenium, Cambridge University Press, 1948, p. 29.
15. B. J. Molnar, P. H. Holloway, and R. E. Hummel, to be published.
16. A. R. Haranahalli, P. H. Holloway, and D. B. Dove, to be presented at 21st Electronic Materials Conference, Colorado, June 1979.

17. R. S. Crandall, P. J. Wojtowicz, and B. W. Faughman, *Solid State Communications* 18, 1409 (1976).
18. J. O. M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, Plenum, New York, 1973, chapters 6 and 7.
19. B. Reichman and A. J. Bard, *J. Electrochem. Soc.* 126, 583 (1979).
20. M. A. Butler, *J. Appl. Phys.* 48, 1914 (1977).
21. L. A. Harris, M. E. Gerstner, and R. H. Wilson, *J. Electrochem. Soc.* 124, 1511 (1977).
22. S. K. Deb and M. Witzke, IDEM Conf., Proc. Intern. Electron Devices Meeting, Washington, D.C., 1975, p. 393.
23. M. Green *et al.*, *Thin Solid Films* 24, 545 (1974); 40, L19 (1977).



Appendix 1  
"Electrochromism in  $\text{WO}_3$  Films with BaO Additions"

# Electrochromism in WO<sub>3</sub> films with BaO additions

B. J. Molnar, A. R. Haranahalli, and D. B. Dove

Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611

(Received 26 September 1977; accepted 10 November 1977)

Films of WO<sub>3</sub> with various amounts of BaO additions were deposited from multiple evaporation sources onto glass substrates heated to 100°C. The atomic percent of Ba in each film with respect to W was determined using particle-induced x-ray emission analysis (PIXIE). Compositional variations with film depth were examined using Auger electron spectroscopy combined with ion beam milling. The electrochromic coloration and decoloration behavior was measured in an electrochemical cell. It was found that additions of Ba as small as 10 at. % measurably reduced the amount of coloration induced per given amount of charge injected into the film. The amount of inhibition of electrochromic coloration was found to increase with increasing Ba concentration. At Ba concentrations greater than 45% the coloration effect was virtually eliminated. Ba additions greater than 45 at. % were also found to induce crystallization in the films.

PACS numbers: 82.45.+z, 78.20.Jq, 61.70.Dx

## I. INTRODUCTION

The phenomenon of electrochromism—the inducement of a reversible color change in a material by the application of a small dc voltage—has received considerable attention during recent years due to the potential application of this effect to electrically alterable, low-power displays suitable for high light ambient and having inherent memory. Most of the published research in inorganic electrochromics has been directed to understanding the effect as exhibited in amorphous thin films of WO<sub>3</sub>, which electrochromically switch from transparent to deep blue.<sup>1-7</sup> Coloration is brought about by the simultaneous injection of electrons and positive ions (most commonly H<sup>+</sup> ions) induced by the application of a small dc voltage (typically 1.5 V) across the film. The electron-injecting contact is commonly a transparent conductive coating on a glass substrate, while the proton injecting contact is usually a dilute H<sub>2</sub>SO<sub>4</sub> solution into which an In or Pt electrode is inserted. The injected charge gives rise to a broad absorption band with a maximum at ~1.38 eV.<sup>6</sup> Reversing the polarity of the applied voltage results in decoloration. It should be noted that WO<sub>3</sub> is also photochromic; i.e., blue coloration can also be induced by ultraviolet irradiation.<sup>1</sup>

The precise electronic mechanism of EC absorption in WO<sub>3</sub> has not been conclusively established. Hollinger *et al.*<sup>6</sup> have proposed that during the electron injection an increase in the number of localized W<sup>5+</sup> states situated ~2 eV above the valence-band edge occurs. These states may give rise to small polaron formation. The absorption results from small polaron transfer<sup>7</sup> or intervalence charge transfer<sup>3</sup> when electrons are excited between W<sup>5+</sup> and W<sup>6+</sup> ions.

One useful experimental approach to the clarification of the absorption mechanism is to study the effect of the addition of various metal-oxide ions on the EC behavior. Ionic additions could for example alter the transition-metal ion site separation and thereby alter the energy at which the absorption maximum occurs. The presence of other transition metal ions could also serve as additional receptors and sup-

pliers of electrons during the excitation process. Faughnan<sup>8</sup> has examined films made by coevaporating WO<sub>3</sub> and MoO<sub>3</sub> (which is also known to be electrochromic).<sup>9</sup> He found that Mo additions cause an increase in the energy of the absorption band maximum, the largest increase being for an addition of 7% MoO<sub>3</sub> ( $E_{\text{max}} = 2.05$  eV). Faughnan used his results to argue in favor of an intervalency transfer model.

In the research discussed in the present paper we have studied the effect of the addition of various amounts of BaO to WO<sub>3</sub>. One stimulus for the examination of the WO<sub>3</sub>/BaO system was the observation by Sakka<sup>10</sup> of photochromic switching of BaWO<sub>4</sub>:Bi(0.1 mol %) powder from white to red. It was thought that the incorporation of BaO in WO<sub>3</sub> films may give rise to interesting results in the EC absorption process.

## II. EXPERIMENTAL PROCEDURE

Mixed-oxide films of WO<sub>3</sub>/BaO of various compositions were deposited on glass substrates, some of which were coated with conducting SnO<sub>2</sub>, by coevaporating WO<sub>3</sub> and BaO powder. The WO<sub>3</sub> was evaporated from an alumina-coated tungsten crucible and the BaO was evaporated from a tantalum boat. During deposition the substrate temperature was 100°C and the pressure in the vacuum chamber was  $4 \times 10^{-6}$  Torr ( $5.3 \times 10^{-4}$  Pa). The average total deposition rate as determined by a quartz crystal monitor was 20 Å/s and the film thicknesses ranged from 0.20 to 0.40 μm.

The atomic percent of Ba with respect to W in each film was determined by PIXIE (particle-induced x-ray emission) analysis.<sup>11,12</sup> Barium additions ranging from 10% to 100% (100% representing pure BaO) were studied. Auger electron spectroscopy equipped with ion milling capability was used to investigate any compositional variations with depth in the film. An x-ray diffraction scan was also made on each film to determine whether or not the film was amorphous. The EC response of each film was studied using the electrochemical cell represented in Fig. 1. A dc potential of 1.5 V was applied

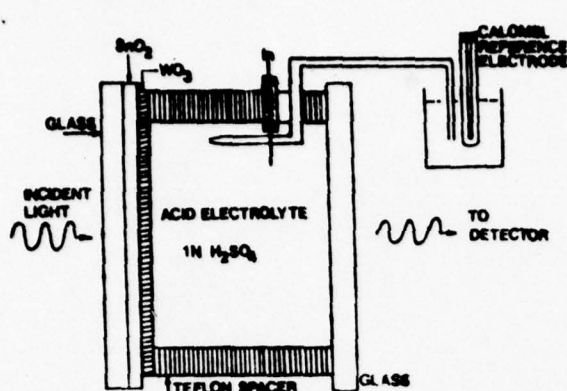


Fig. 1. Schematic of the electrochemical cell used to electrochromically induce coloration and decoloration in  $\text{WO}_3/\text{BaO}$  thin films.

across the  $\text{SnO}_2$  and In electrodes. The In electrode was immersed in a 1N  $\text{H}_2\text{SO}_4$  solution. The transmitted intensity of an incident monochromatic beam of red light (1.80 eV) was measured as a function of coloration and decoloration time. A representative curve for  $\text{WO}_3$  and for  $\text{WO}_3:\text{Ba}$  (10%) is shown in Fig. 2(a). The current through each film during coloration and decoloration was also measured as shown in Fig. 2(b).

### III. EXPERIMENTAL RESULTS AND DISCUSSION

Addition of BaO to films of  $\text{WO}_3$  was found to have an inhibiting effect on their coloration ability. For example, Fig.

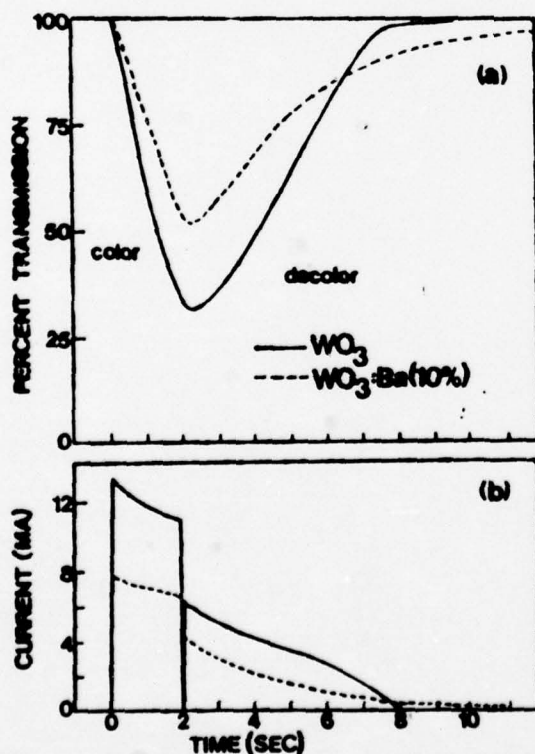


Fig. 2. (a) Percent transmission of monochromatic red light (1.80 eV) through a  $\text{WO}_3$  and a  $\text{WO}_3:\text{Ba}$  (10%) film, respectively, as a function of coloration and decoloration time for 1.5 V applied across the  $\text{SnO}_2$  and In electrodes. (b) corresponding variation of current through the respective film during coloration and decoloration.

54

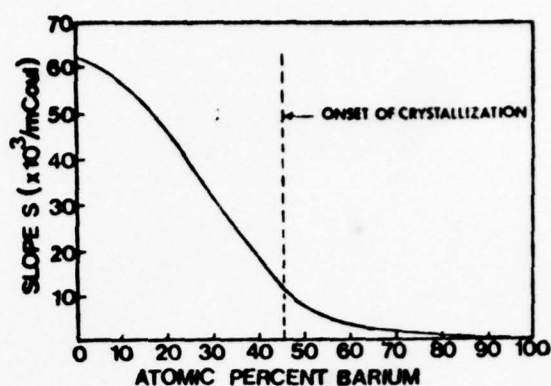


Fig. 3. Variation of slope  $S$  of  $\ln(I_o/I)_t$  vs  $(f dt)_t$  with Ba concentration in  $\text{WO}_3/\text{BaO}$  films.  $S$  is a measure of the amount of coloration induced for a given amount of charge injected.

2(a) shows that addition of 10% Ba reduces the total amount of light absorbed electrochromically in comparison to pure  $\text{WO}_3$ . A measure of the amount of coloration induced for a given amount of charge injected is given by the slope  $S$  of a plot in  $\ln(I_o/I)_t$  vs  $(f dt)_t$ , where  $(I_o/I)_t$  is the ratio of incident light intensity to transmitted light intensity after coloration time  $t$  and  $(f dt)_t$  is the area under the current-time curve after time  $t$ . The variation of  $S$  with Ba concentration is shown in Fig. 3. It is seen that the ability to inhibit coloration increases with increasing Ba concentration. For Ba concentrations up to 10% the coloration inhibition is small. For Ba concentrations greater than 40%, however, the inhibition is almost total. The form of the  $S$ -vs-concentration plot was not found to vary significantly with wavelength of the incident light in the range 1.1–1.8 eV. It should be noted that those films with ~10% Ba were found to have a deep blue coloration upon removal from the vacuum system. This coloration was removed by application of a decoloration potential of 1.5 V. Such coloration in the virgin condition was not observed in any of the pure  $\text{WO}_3$  film or in films with Ba concentrations much greater than 10%. Sharp peaks were found to emerge in the diffuse x-ray diffraction patterns of the films at Ba concentrations greater than ~45%, indicating the onset of crystallization. The amount of crystallization was found to increase with increasing Ba concentration. It is believed that the presence of crystallites is at least partly responsible for the coloration inhibition in these films with the higher Ba concentrations. Further experimental work is necessary for the elucidation of the coloration inhibition at lower Ba concentrations. One possible explanation, however, is that the Ba addition increases the tungsten ion site separations sufficiently to decrease the probability of optically induced excitation between these ions. Auger electron spectra obtained for selected films indicated that the tungsten, barium, and oxygen concentrations did not vary significantly with depth into the films.

### ACKNOWLEDGMENTS

The authors would like to thank F. Ohuchi for obtaining the Auger spectra and H. A. Van Rinsvelt, J. A. Guffey, and J. Sanders for performing the PIXIE analysis. This research



was supported by ARO, Durham under Contract No. DAAG29-76-G-0151.<sup>55</sup>

<sup>1</sup>S. K. Deb, *Philos. Mag.* **27**, 801 (1973).

<sup>2</sup>B. W. Faughnan, R. S. Crandall, and M. H. Lampert, *Appl. Phys. Lett.* **27**, 275 (1975).

<sup>3</sup>B. W. Faughnan, R. S. Crandall, and P. M. Heyman, *ACA Rev.* **26**, 177 (1975).

<sup>4</sup>H. N. Hersh, W. E. Kramer, and J. H. McGee, *Appl. Phys. Lett.* **27**, 645 (1975).

<sup>5</sup>L. F. Chang and W. E. Howard, *IEEE Trans. Electron. Devices* **ED-22**, 740 (1975).

<sup>6</sup>G. Hollinger, T. M. Duc, and A. Deneuville, *Phys. Rev. Lett.* **37**, 1564 (1976).

<sup>7</sup>O. F. Schirmer, V. Whitler, G. Baur, and G. Brandt, *J. Electrochem. Soc.: Solid-State Sci. Technol.* **124**, 749 (1977).

<sup>8</sup>B. W. Faughnan, Paper 422 presented at the Electrochemical Society Spring Meeting, Washington, DC, 2-7 May 1976.

<sup>9</sup>T. C. Arnoukhusen, *J. Electrochem. Soc.: Solid-State Sci. and Technol.* **123**, 527 (1976).

<sup>10</sup>S. Sakka, *J. Amer. Ceram. Soc.* **82**, 60 (1969).

<sup>11</sup>A forthcoming paper will deal with the application of PIXIE to the analysis of thin films of WO<sub>3</sub> with various additives.

<sup>12</sup>For a set of recent papers on PIXIE see the "Proceeding of the First International Conference on PIXIE Analysis", *Nucl. Instrum. Methods* **148**, 1 (1977).



Appendix 2  
Project Personnel

Dr. Derek B. Dove served as the project's Principal Investigator until he left the University of Florida for IBM, Yorktown Heights, NY, in August 1977. Since that time, Dr. Rolf E. Hummel has been directing this research as a principal investigator.

Dr. Hummel has had experience with optical and electrical properties of metals and alloys since 1958. He has developed, at the University of Florida, the differential reflectometer, which has been used for this research and which is capable of precisely measuring the transmissivity and reflectivity of electrochromic devices. Dr. Hummel is the author of a book entitled Optical Properties of Metals and Alloys, which was published in 1971 in the series *Reine Und angewandte Metallkunde in Einzeldarstellungen* (monographs in Pure and Applied Metallurgy) by the Springer Publishing Company. Dr. Hummel teaches courses in optical properties of metals, electron theory of metals, and electrical and magnetic properties of metals and semiconductors. Professor Hummel also has experience in thin film technology through his project on "Electro-transport in Thin Films," which has been supported for ten years by NASA and the Air Force.

Dr. Holloway has served as a co-principal investigator on the project since August 1978. He has worked with the physical and chemical properties of surfaces and thin films since 1969. His work has emphasized the study of these properties using materials characterization techniques

involving electrons in both core and valence levels. He is the author of 45 publications and reports related to his past activities. He is currently directing research on the effects of composition and structure upon the efficiency of polycrystalline silicon photovoltaic devices. This detailed correlation between composition, microstructure, and electrical properties is very complementary to this research project.

Two graduate students have been working on this project, Mr. A. R. Haranahalli and Mr. B. Molnar. This research will form the basis for their doctoral dissertations. Mr. Haranahalli will graduate in March 1980, and Mr. Molnar, who has worked on the project for the past three years, is expected to graduate with a Ph.D. in August 1979.

Appendix 3  
Publications and Presentations

Publications

B. J. Molnar, A. R. Haranahalli, and D. B. Dove, "Electrochromism in  $WO_3$  Films with  $BaO$  Additions," J. Vac. Sci. Technol. 15, 261 (1978).

Presentations

- \* B. J. Molnar and D. B. Dove, "Electrochromism in  $WO_3$  Films," 19th Electronic Materials Conference (AIME), June 1977, Ithaca, NY.
- \* B. J. Molnar and D. B. Dove, "Electrochromism in  $WO_3$  Films with Atomic Additions," 24th National Symposium of the American Vacuum Society, November 1977, Boston, MA.
- \* A. R. Haranahalli, P. H. Holloway, and D. B. Dove, "The Influence of Metal Overlayers on Electrochromic Behavior of  $WO_3$  Films," 21st Electronic Materials Conference (AIME), June 1979, Boulder, CO.